## METALS AND ALLOYS

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Number 8

August, 1936

## The Magazine of Metallurgical Engineering

PRODUCTION TREATMENT

FABRICATION APPLICATION

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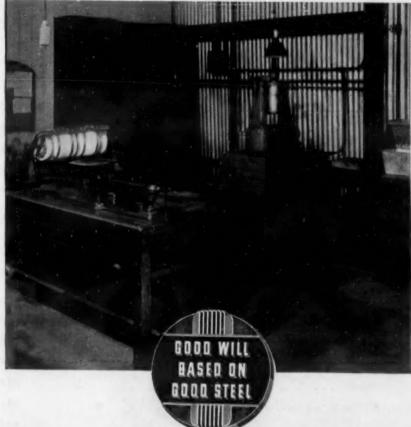
#### CURRENT METALLURGICAL ABSTRACTS

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#### MODERN PROCEDURE IN ALLOY STEEL PRODUCTION

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Ceramics—in the form of refractory materials—play an important part in modern alloy steel manufacture. The nature and quality of the materials used for lining furnaces, ladles and metal hot tops have definite influence on both the quality of the steel and the cost of production.

Recognition of the importance of refractories is seen in the Timken Ceramic Research and Testing Laboratory, two views of which are shown.

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Testing refractories is another valuable function of the laboratory. All refractory material purchased from outside sources is subjected to searching tests before being passed for use—and the required standard is high.

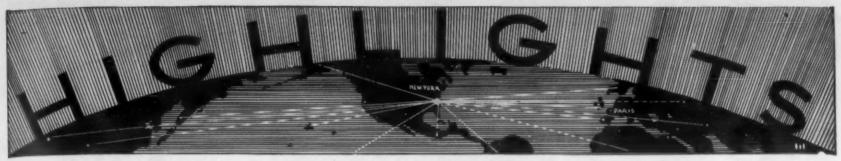
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#### Written by the Abstract Section Editors and the Editorial Staff

Do YOU want to know what metallurgical engineers are saying, the world over? Look in the Current Metallurgical Abstracts. Here are some of the points covered by authors whose articles are abstracted in this issue.

#### Flue Dust and Gases Now Blamed

Much has been blamed on the weather man and the weather; now it is the amount of flue dust formed in blast furnaces and the composition and heat content of the gases (page MA 396 R 6).—A.H.E.

#### Carbon-Oxygen

If you want to get the German view-point on oxidation of open hearth steel, see Körber and associates' summary of a large number of investigations (page MA 397 R 2).—C.H.H.

#### Still a Debated Question

The opinion of thirty open hearth operators, as gathered and reported by Cone (page MA 405 L 2) indicate varying benefits derived from the insulation of open hearth furnaces.—M.H.M.

#### A Zn-Cd Alloy As a Solder

Morrough (page MA 407 L 2) advocates 60 Zn 40 Cd as a solder for Al.—H.W.G.

#### Cobalt High Speed

The role of Co in high speed steel is none too clear, but Kojima (page MA 413 L 2) thinks its presence may favor the formation of a stable tungsten carbide.—H.W.G.

#### Deep Etching

Houdremont and Schrader (page MA 413 L 3) believe that steel specimens should always be quenched and drawn before applying the deep etch test.—H.W.G.

#### Savings from Scrap Piles

One fruitful method of effecting savings through welding and cutting in almost any plant is by reclamation of worn, cracked or broken parts from the scrap pile. Any experienced welder can inspect the average scrap pile and find dozens of pieces of equipment which can be salvaged by building up, welding or cutting.

As a matter of fact, pieces repaired

in this manner often can be made stronger and more durable than new parts. Frequently a high-strength welding rod, which makes the weld the strongest section of the entire piece, may be used. This practically eliminates the possibility of repetition of fracture at the same point at least.

Then too, if a hard-facing material or wear-resisting alloy is used to build-up worn surfaces which are exposed to severe wear in service, the hard-faced part will outlast a new plain part many times.

Economies obtainable by using material from the scrap pile to fabricate welded constructions required around the plant likewise are considerable in the majority of cases and well worth looking into (page MA 407 L 7).—E.V.D.

#### Zinc Base Bearings

Prever (page MA 416 R 4) discusses Zn-base bearings for use when political conditions as in Italy and Germany impose restrictions on the use of Sn, while Welter and Brasch (page MA 421 L 4) deal with very high pressure lubricating systems aimed to make the Zn alloys useful.—H.W.G.

#### Loss or Gain in Cupola Melting

An answer to the problem as to the actual loss or gain in cupola melting is offered by Lannigan (page MA 397 R 6). The carbon pick-up or gain in steel, minus the total of pig and scrap, left a net gain of 1 per cent.—E.F.C.

#### Hotter Cupola Iron at the Spout

To raise the temperature of the iron at the spout of the cupola, Murphy (page MA 406 R 6) used petroleum coke having a high fixed carbon. Temperature was advanced from about 2400 to as high as 2700 to 2750 deg. F.—E.F.C.

#### Cd in Place of Sn in Solders

Here is a suggestion for saving tin. Eyles (page MA 407 L 6) finds that a lower tin content is not detrimental in many joining solders. He recommends Cd as a substitute. Interesting metallurgically, but what about the cost?— E.F.C.

#### Stainless Steel by a New Process?

A new chromizing process, developed by a Cleveland company, is described as producing a product, when applied to mild steel, which has all the desirable properties of stainless steel (page MA 411 L 10). A casing of ferrochromium is formed on the steel containing 25 to 30 per cent Cr.—E.F.C.

#### More Data on Heat Resisting Alloys

Apparently valuable data on certain heat-resisting alloys are disclosed by Murphy (page MA 416 R 7). He gives prominence to the 80 Ni-20 Cr alloy and compares it with the cheaper one, 65 Ni, 20 Fe, 15 Cr. Production of the 80-20 product is pronounced one of the most difficult present day metallurgical tasks.—E.F.C.

#### Aluminum Resists Alcohol

Lühder (page MA 421 L 5) reports that apparatus made of aluminum has been successfully used in the distillation of alcohol in Germany in applications where bronze had failed.—E.F.C.

#### Impurities in Bearing Metals

Stating that impurities exert a powerful effect on the structure and physical properties of bearing metal alloys for internal combustion engines, Bassett (page MA 421 R 4) offers valuable data. Information on the effects of Pb, Ni, Zn, Al and Bi is included. To each of these some detrimental effect is ascribed.— E.F.C.

#### Low Alloy Steels for Bridges

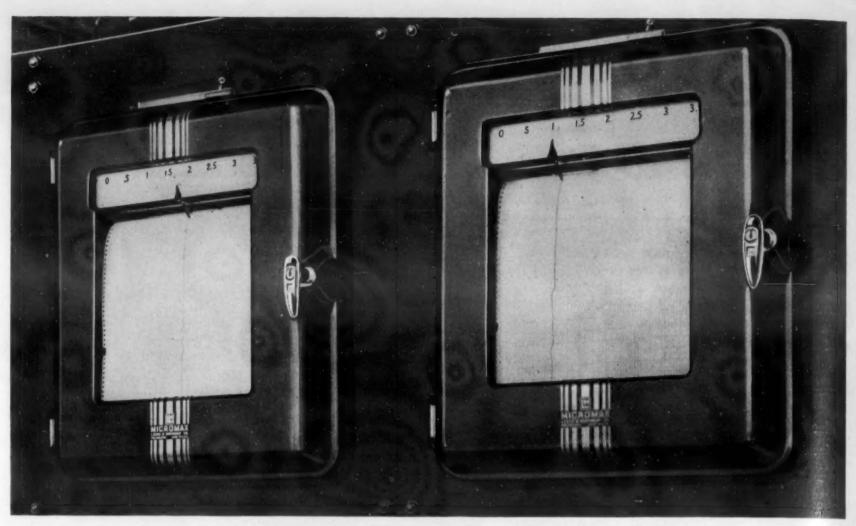
That a series of studies of alloy steels for American bridges containing Cu, Cr, Mn, Ni, Mo, Si or V, may result in changes in design is the testimony of an English writer (page MA 422 R 5). Sounds very much like the possible larger use of the low alloy, high elastic steels. The employment of the Ni and medium Mn steels is cited.—E.F.C.

#### How to Obtain Quality Steel Castings

Advice as to the best way to obtain quality steel in castings is given by Collier (page MA 423 R 6). He deprecates hand-to-mouth buying which often results in a sub-standard product. Emphasizing that time is essential in making good castings, he advises users to anticipate as far as possible their requirements.—E.F.C.

#### Industrial Uses of Silver

Addicks (page MA 421 R 3), a well-known authority, discusses at length the use of Ag for bactericidal purposes. He also includes Ag as a corrosion resisting metal, Ag in alloys and silver commutators.—E.F.C.



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#### Our Section Editors

(Continued from the July Issue)

ERNEST V. DAVID is connected with the applied engineering department of the Air Reduction Sales Co., New York. Though a native of Greenville, S. C., he received his M. E. degree from Winterthur Technikum, Switzerland. He has also an E. E. degree from the Massachusetts Institute of Technology.

Mr. David served with the Newport News Shipbuilding & Dry Dock Co., as a marine engineer draftsman from 1912 to 1915 and with the Fore River Shipbuilding Co. as a submarine inspector from 1915 to 1917. Other connections include service as an engineer officer in the Navy from 1917 to 1919; as a sales engineer with the General



ERNEST V. DAVID

Electric Co., in Buenos Aires, 1920 to 1922; as a marine engineer with the shipping Board from 1922 to 1927 and as production manager with the F. E. Pendleton Co. from 1927 to 1929, when he assumed his present position.

Mr. David is a licensed professional marine engineer. He is a member of the A.S.M.E., the A.W.S. and the International Acetylene Association. He was general chairman of the oxyacetylene committee of this association during 1935. Several papers on welding, cutting and

metal spraying have been delivered by Mr. David before these technical organizations.

A. W. DEMMLER is metallurgical engineer in the research and development department of the Vanadium Corp. of America at Bridgeville, Pa. He was promoted to this position early this year. He was graduated from Penn State College in 1919.

In 1920 Mr. Demmler obtained the degree of M.S. in electrochemical engineering from the Massachusetts Institute of Technology. He continued his graduate studies at the Royal Technical University at Stockholm, Sweden, as fellow in electrometallurgy of the American-Scandinavian Foundation. He also obtained practical experience in some of Sweden's industrial plants.

Upon his return to this country he taught applied electrochemistry and electrometallurgy at Penn State College and later en-



A. W. DEMMLER

tered the industrial field in the metallurgical department of the United Alloy Steel Corp. About 13 years ago he joined the Vanadium Corporation and grew with the research and development division to his present position.

ALDEN H. EMERY is assistant manager of the American Chemical Society. He was graduated from Oberlin College, Oberlin, Ohio, in 1922. The following year he took his M.A. degree at Ohio State University, Columbus. Further graduate work was pursued at George Washington University, Washington. He is a member of Phi Beta Kappa and Sigma Xi.

In 1923 Mr. Emery joined the staff of the U. S. Bureau of Mines at Pittsburgh. In 1927 he was made assistant to the chief engineer of the Experiment Stations Division in Washington. Subsequently he became assistant chief engineer of the division



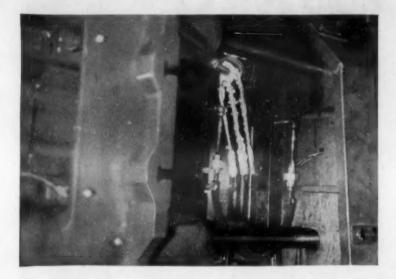
ALDEN H. EMERY

from which position he resigned last January to assume his present connection. He has served as an assistant editor of Chemical Abstracts since 1928 and has been associated with METALS AND ALLOYS since its establishment.

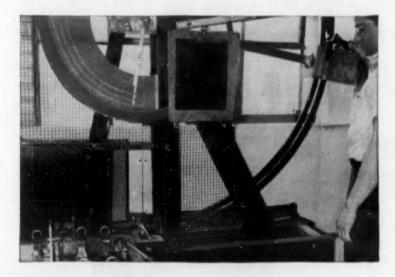
Mr. Emery is a member of the American Chemical Society, the American Institute of Mining and Metallurgical Engineers, the American Mineralogical Society and a Fellow of the American Association for the Advancement of Science.

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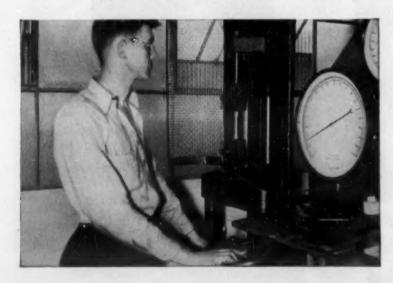
#### TEST BARS ARE DIE CAST UNDER

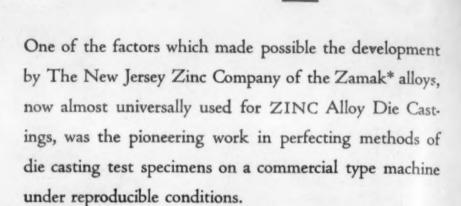


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## PHYSICAL PROPERTIES DATA





Having developed suitable methods of testing, it was necessary to carefully study some 400 separate alloy compositions in order to determine the effects of the seven elements mentioned in the specifications for the Zamak alloys. The discovery of the effect of casting variables on a single property has frequently involved casting and testing thousands of individual specimens under rigidly controlled conditions.

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The complete data on these alloys are available in our Research Bulletin, "Zamak Alloys for Zinc Alloy Die Castings." We will gladly send you a copy on receipt of a request on your company letterhead.

\*Registered trade-mark. The formulas for these alloys are covered by patents owned by The New Jersey Zinc Company. Licenses to make ZINC alloys with HORSE HEAD SPECIAL (99.99+%) ZINC under these patents have been granted to a number of manufacturers of alloys and certain commercial die casters who make their own alloys.

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#### X-Rays As a Tool

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THE two-day Symposium on "Radiography and X-ray Diffraction Methods" held at the A.S.T.M. meeting, June 30 and July 1, was misnamed. Relatively few people care just what the details of the methods are; they leave those to the experts who use X-rays. But a lot of people do care whether the use of the up-to-date methods, whatever they are, helps the engineer and the metallurgist to make things stronger, better and cheaper.

Fortunately the authors of the dozen papers in this symposium took a broader view of the subject and instead of merely setting forth the details of satisfactory technique, (which are discussed, too, as of course they should be) they deal even at greater length with what X-ray methods are good for, and what kind of problems they can lick.

This engineering attitude is especially notable in the six papers on radiography including both X-rays and gamma-rays, where industrial authors outnumber the professional ones five to one. The nondestructive testing of welds and the use of radiographs, first on pilot castings or to show what gating will give best results, and finally as an inspection test, are clearly brought out. All these papers are good, but Lester's is a hum-dinger. He deals with specifications for soundness under X-ray inspection and raps those who impose such a specification without clearly stating just what type and location of defects will be cause for rejection. Under the searching eye of the X-ray, many a casting that looks nice on the outside is found unsound on the inside and, in general, the problem is how to chase the defects into the places where they don't count and away from those in which they do harm. All these articles have a mighty sound and realistic point of view.

The summaries of these papers, if read by engineers and executives, will do much toward increasing the use of radiographic pilot testing and inspection testing, and in making for a commonsense, engineering utilization of the methods.

Several of the papers in both sections of the symposium are worked up by the author from data and comments supplied by several others, so that the information is based upon the experience of many more than just the authors themselves.

The six X-ray diffraction papers show a preponderance of professors to technical users, the ratio being 5:1, and so have a more high-brow slant than do those of the other session. Yet these too, while dealing partly with how it ought to be done, are chiefly concerned with what the methods can show when they are correctly applied. Cases in which one may get additional corroborative data as to what's in an alloy from the point of view of

structural constituents and, to some extent, of chemical composition are clearly set forth. Moreover, the limitations are brought out as well as the possibilities.

A picture is given of what can be told about coldworked metals by diffraction methods, of the approximation or semi-quantitative evaluation of particle size, and of the information that can be secured on preferred orientation.

So many of the individual articles in the literature on diffraction methods are so highly technical that they are hard reading and the non-specialist trying to follow them can't see the woods for the trees. It is very much worth while to have a summary of this sort. The pamphlet in which these dozen articles will finally be published will be much easier reading than most books on the subject, and should be in the library of every metallurgist even when there doesn't seem to be the remotest chance that he will himself be called upon to use X-rays. He will see those cases in which X-ray information can serve him, can pass them over to an expert to handle for him, and can get a pretty intelligent idea of how to interpret the findings, from a study of the symposium.

The word "methods" in the title of the symposium shouldn't scare off those who are not among the elect of the experts in this field, for the whole discussion is good information for the run-of-mine engineer and metallurgist.—H.W.G.

#### **Expansion in Die Castings**

NE of the rather remarkable developments during the past five years of depression in industry has been the expansion of the American die casting industry. According to data recently released by the American Bureau of Metal Statistics, there were 51,021 tons of metal consumed in 1935 in the manufacture of these products. These data are from about 75 per cent of the industry on the basis of zinc. With the exception of 1932, the bottom of the depression, there was a steady increase from 1931 to 1935, or from 19,992 tons in 1931 to the 51,000 tons last year. The actual data were 15,705 tons in 1932, with 24,180 tons in 1933 and 30,241 tons in 1934. Thus the expansion for the five years from 1931 to 1935 was about 161 per cent. Among the metals used in this industry zinc naturally occupies the major position, having been 41,560 tons in 1935, or 81.5 per cent of the total. Consumption of zinc in the five years expanded 175 per cent. Aluminum and copper ranked next at 7,625 tons and 1,077 tons respectively. In contrast to the struggles of many other industries in which the trend in production and consumption was decidedly in the other direction, the expansion in the use of alloys for die castings is impressive.—E.F.C.

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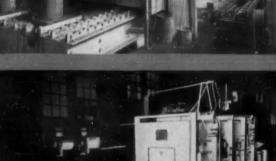
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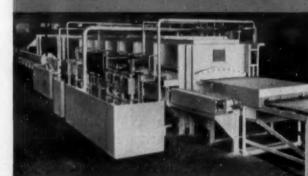
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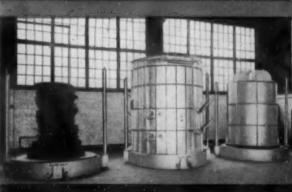
Clean Hardening (Controlled Atmospheres)



#### ANNEALING

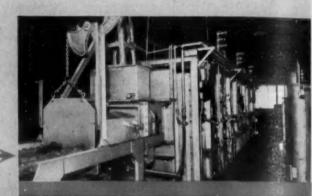
Bright Annealing
(Controlled Atmospheres)

Direct heat,

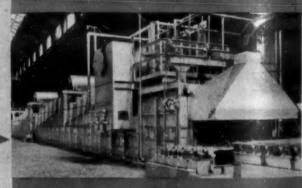


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## Some Properties of Nickel Electrodeposits

By ROBERT J. McKAY

Development & Research, International Nickel Co., New York

given to certain specific nickel plating developments. The newly improved facility of producing a bright deposit, the production of soft deposits which are as ductile as the steel base, the ability to plate at current densities as high as 300 amp. per sq. ft., the production of deposits with a hardness greater than can be obtained by cold rolling, and of deposits with considerable thickness, each has its special application. The relation of each product to the others and to the baths which produce them constitutes an interesting mosaic. It is the purpose of the present paper to outline this general pattern rather than to dwell on any particular one of these useful properties.

The consistency, if not the completeness, of the final picture is a tribute to the general development of electroplating during the last decade or so from a rather crude art into a reliable scientific procedure. The older empirical rules which, when closely followed, produced deposits of passable appearance, physical

properties and protective value, tend now to give way to an intelligent and varied procedure which gives a range of properties, including the best obtainable by the old procedure along with certain new features. Many of the controlling factors have been covered by publications and it is possible to draw up a general, though only partially complete, set of relations between plating baths and their conditions on the one hand and the resultant properties of the electrodeposits on the other.

Naturally, with increased knowledge the control of cost factors has improved and present practice produces good deposits at lower cost than the old.

#### Part I \_ Process Control

Hydrogen ion Concentration: Different acids at the same concentration display different activities and are therefore spoken of as "strong" or "weak." Hydrogen ion concentration is easily and correctly under-

Modern Automatic Plater for Automobile Parts. (Courtesy Hanson-Van Winkle-Munning Co.)



August, 1936-METALS & ALLOYS

5

Nickel Electrodeposition Tanks, 6 Acres in Area. International Nickel Co., Inc., Port Colborne, Ont.



stood as the activity (or "strength" in the above sense) of the acid. It is now commonly referred to as pH because this symbol gives a simple series of reference numbers. [In a note at the end of this article the author gives his definition of pH for the benefit of those interested.]

It seems to the writer that the truly scientific development began with the realization by the physical chemist some years ago of the relation and difference between pH or acid "activity" and the gross concentration of acid. Thompson<sup>1</sup> in 1922, described the importance of the pH value of plating baths. Above a certain pH, nickel will precipitate from most solutions as a hydrate. At lower pH the voltage necessary to deposit molecular hydrogen is less than that for nickel, and therefore a nice adjustment of the hydrogen ion concentration is necessary to the production of good electrodeposits. If the pH is too high, the deposit is harmed by precipitation of nickel hydrate, and if too low, molecular hydrogen is deposited at the expense of nickel. The thin film of liquid at the cathode is at higher pH than the body of the solution and must be replenished by convection and diffusion.

At about the same time as Thompson's work, it was noted in the process of electro-refining of nickel that the hydrogen ion concentration bore a rather definite relation to the current densities which produced sound nickel, with some modification due to the circulation rate and other factors. The current efficiency of nickel deposition is lower at low current densities and at low pH, because then a larger part of the current is used to change hydrogen ions to gaseous hydrogen.

The improvement in plating noted in the presence of certain weak acids (known as buffers) such as boric acid and acetic acid, is explained quite simply by their action in raising the pH for any given gross acidity. In their presence, a large change in total acidity produces a small change in pH, and therefore the pH in the cathode film remains constant and under control, even when appreciable quantities of hydrogen gas are deposited by electrolysis. As will be seen later, even the properties of what would be called "good" electroplate will depend on the pH. At the present time, reliable and quick methods are available

for determination of the pH value and are important factors in the control of properties.

The range of pH 2 to pH 6 covers the average varieties of baths. Rather paradoxically, as a result of the knowledge of the effects of hydrogen ion concentration, useful methods of plating have been developed which allow a variation many times greater than in old practice; and a knowledge of the effect of buffers has enabled us to plate without buffers under some conditions.

Current Density: The current density affects the properties of the plate and is one of the principal factors that determines costs, as the time of doing any given job varies inversely, and the power used varies directly, with the current density.

As the current density increases, the amount (but not the proportion) of hydrogen plated out increases and hence the pH at the cathode is raised. Hence, high current densities are best used in solutions of low pH. In the older plating baths, the solutions were nearly neutral and current densities were necessarily low. With definite hydrogen ion control, the current densities need not be held to close limits. A current density of 10 amp. per sq. ft. was a reasonably high figure in the "horse and buggy" days, while now it is a common practice to plate automobile parts at 50 amp. per sq. ft. Several investigators have reported on higher current densities, and the possibilities are well illustrated in recent work of Blum and Kasper.2 Under the rather unusual conditions of pH 1 to 2 and boiling temperatures, nickel deposits of quite good properties were produced at current densities from 200 to 400 amp, per sq. ft. The operating problems become more difficult at such current densities.

Apart from the cost factors mentioned, high current densities may be desirable or undesirable for a given purpose. Their effect on physcial properties and appearance is not yet entirely clear, and it depends on the constituents of the bath as well as the other ordinary variables. The advantage of changing the rate of plating is illustrated by the fact that, while the older maximum of 10 amp. per sq. ft. would produce a thickness of only 0.0005 in. in an hour, the new maximum of 400 amp. per sq. ft. will produce this

coat, which is protective in mild atmospheres, in one minute and a half. To look at this from another angle, the high current density would produce a 25

gage sheet in one hour.

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Rate of Movement: The former tendency to use still baths and cathodes is being superseded in many quarters by continuous processes of mechanical handling and even by deliberate agitation of the bath. The relative movement of the bath and the cathode determines how much the cathode film varies from the body of the solution. Therefore, a high rate of movement tends to make conditions more uniform at the cathode. It is also easier to control a reasonably rapid movement than to maintain absolute stillness. The practical use of agitated baths seems more common in Europe than in America.

The disadvantages of agitation are mainly: (1) the additional apparatus necessary to maintain it and (2) the tendency to bring any floating particles into contact with the cathode and thus damage the plating.

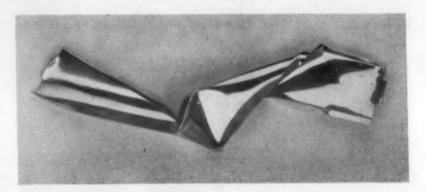
Cleanliness: Anode sludge or other floating particles are detrimental when they reach the cathode. Where reasonable quiet is maintained, clear solutions can be obtained by settling. In agitated or rapidly moving baths a portion of the solution may be withdrawn continuously and mechanically filtered. Freedom from all foreign particles, except certain colloidal materials, is most desirable.5 Recent improvements in filtering methods, anode bags and screens and in methods of cleaning the base metals leave little need for trouble from this source in modern baths. Much pitting due to floating particles has been eliminated by careful cleaning of the solutions and cathodes. Cleanliness of the surface to be plated has been found to be the major essential for adherent deposits. Efficient cleaners and pickling solutions have quite fully removed the fear of separation or exfoliation.

Temperature: Nickel deposition can be carried out at any temperature from room temperature to the boiling point of the electrolyte. The temperature is easily controlled except at high current densities, and it has certain definite effects on properties. Some practical limitations are imposed by the materials suitable for

Oxidation: A former bugbear of the practical plater was pitting of the deposit. While the underlying cause of this may be either floating particles or conditions on the surface to be plated, English investigators<sup>3, 4</sup> believe that it is always connected with the adherence of electrodeposited molecular hydrogen.

handling the corrosive electrolytes.

others have been used successfully. By adding a sufficient quantity, the hydrogen bubbles can be completely prevented from forming, but small additions are usually sufficient. In general practice the underlying cause of pitting is the presence of floating particles. After proper purification in such cases peroxide additions are unnecessary. These positive cures for a troublesome defect have been most useful in maintaining high quality deposits under various conditions.

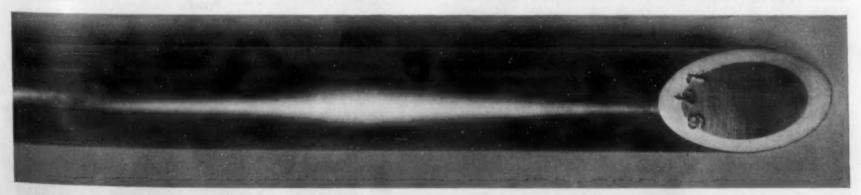


Steel Strip, 0.016 In., "Bright" Plated with 0.001 In. Nickel. Deformed to illustrate ductility. (Courtesy Hanson-Van Winkle-Munning Co.)

Composition: The materials used in electroplating baths may vary within wide limits and general statements regarding them are likely to be misleading. The common salts, nickel chloride and nickel sulphate, are the basis of most solutions. Alkali metals, particularly potassium, may be introduced for special purposes and ammonium salts have their definite use as buffers and hardeners. Several weak acids are useful buffers, the most common being boric acid and acetic acid. Fluoride baths have special properties with difficultly soluble anodes and serve as exceptionally good buffers in an intermediate pH range. Nickel has been deposited from strongly ammoniacal solutions. Here again, as with the other variables, appears a wide range of conditions from which nickel may be deposited if proper control is exercised.

#### Part II \_\_ Properties of the Product

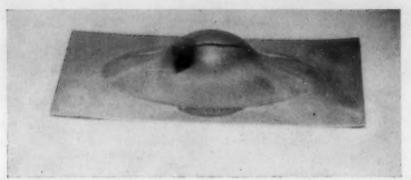
N THE above discussion of plating bath control no attempt is made to cover those details which would be of interest only to electroplaters. The properties of



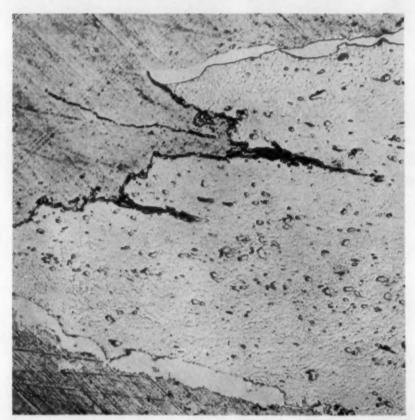
Steel Shaft Built Up with 1/8 In. Pure Nickel and Lathe Turned (4/3 Natural Size.)

Where conditions are such that hydrogen bubbles adhere for some time or form repeatedly on the same point, pits result. An obvious and positive cure for this condition is the addition of oxidizing agents which decrease the evolution of hydrogen. The usual oxidizer is hydrogen peroxide which does not introduce any foreign materials as reaction products; but several

electrodeposits depend on the conditions of deposition, and the purpose of the foregoing paragraphs has been to outline the principal variables which govern the properties of the deposit. The following section describes the properties which can be obtained, showing where possible the connection between properties and plating conditions. While we cannot draw



Erichsen Test of 0.010 In. Steel Sheet with 0.0003 In. Nickel Plate.



Section Through Erichsen Break Above Showing Satisfactory Adherence at Fracture. Magnification 500 diameters.

up a complete theory of practice and resultant properties, those properties which are under some control show interesting general relations.

Certainly the idea that electrodeposited nickel has certain peculiar and closely defined properties is no longer tenable. Its properties vary in as wide a range and are almost as reproducible as those of cast or rolled metal. Many electrodeposited metals are harder than other forms of the same metal or alloy. For instance, chromium plate is noted for its hardness. Hard, brittle and porous nickel plates have been made, owing to uncontrolled conditions, but nickel can be deposited at will in a range of hardness from well above that of the rolled metal to a softness almost equal to the fully annealed metal. There is no more reason to expect physical defects in electrodeposited nickel than in any other form.

Thickness: Nickel electrodeposits have a certain advantage over rolled material in the facility with which thin deposits can be obtained. A deposit as thin as two hundred-thousandths of an inch will present a uniform appearance to the eye. Any thickness from this point up to heavy sheet mill gages can be electrodeposited in proper baths. There is no positive penalty on low thickness, such as there is in the case of rolled sheets, where the extra rolling on light gages produces such a cost differential that light sheet may cost even more per square foot than heavier. However, closer control of conditions is necessary for heavy plating and the difficulty of obtaining a smooth surface increases with the thickness.

Notwithstanding this fact, research workers now use such typical thicknesses as 0.014 in.4 or 0.024 in.2 for the determination of properties and platers advertise thicknesses as high as 7/32 in. Such thicknesses are, of course, entirely unnecessary for ordinary weather protection. Modern specifications give 0.0075 in. as the minimum thickness for nickel electro-deposits as applied on a steel base and 0.0004 in. for mild conditions. These thicknesses are considerably greater than older practice and have been proven by thorough test to be satisfactorily resistant to a range of atmospheres. With present knowledge of bath control they are readily and inexpensively applied. Thinner coats are, of course, less protective. Electrodeposits, however, seem, contrary to former belief, to be just as dense and free from pores as hot dipped coatings.

The data in Fig. 1 give the number of pores as determined by independent workers on tin<sup>7</sup> and nickel<sup>8</sup> coatings on steel using different methods for determining porosity. Such counts are somewhat a matter of judgment, and particularly when they are determined by different investigators with different methods, exact comparisons are questionable. However, the data furnish an indication that electrodeposited nickel is rather less porous than hot dipped tin. Recent tests by both the ferroxyl and hot water method, made in the laboratories of the International Nickel Co., have confirmed these results.

The protective value of either a hot dipped or electrodeposited coat seems to depend on the presence of a certain minimum thickness and the realization of this, in the preparation of the specifications mentioned, is a sound advance.

Reflectivity: One of the present uses of nickel electrodeposits is as a protective undercoat for decorative chromium finishes. For this use as well as when nickel is used as an independent protection and metal finish, the expense of obtaining a brilliant finish is lowered if brilliancy is obtainable directly in the plating bath. It has been known for some time that certain organic and metallic additions to the bath will tend to produce this brilliancy. Commercial use has long been made of such materials as gum tragacanth, licorice and cadmium salts. Brilliancy has also been apparent under certain specific conditions of the common variables

Fig. 1. Porosity of Coatings of Hot-Dipped Tin and Electrolytic Nickel at Varying Thicknesses.

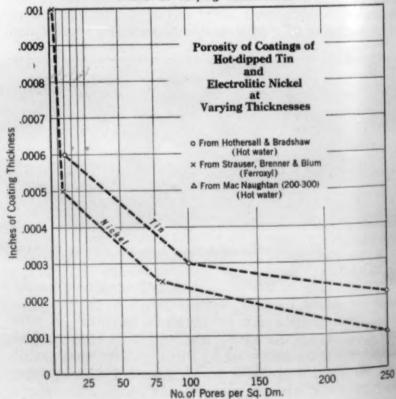


Table 1.—Hardness and Microstructure of Electrodeposited Metals<sup>o</sup>

		Range of Characteristics so far Det	stics so far Determined		Brinell	ardness	
Metal Chromium	Solution Chromic acid	Brinell or Diamond Pyramid Hardness 400-950	Microstructure No definite structure	Factor Chiefly Responsible for Variation Observed Temperature, current density	Of Fully Annealed Metal 70	Of Work- hardened Metal	
Platinum *		606-642	Not available		47	97	
Rhodium *		594-641	Not available		101		
Palladium *		190-196 385-435	Not available Not available		49	109	
Nickel	Sulphate with additions of various salts	125-420	Soft deposits — columnar crystals	pH	70	300*	
	With addition of or- ganic colloids	Up to 550	Hard deposits—no defi- nite structure	Presence of colloids	***	***	
Cobalt	Sulphate with additions of various salts	164-380	Similar to nickel for equal hardness	pH	86	***	
Iron	Sulphate chloride	140-350	Similar to nickel for equal hardness	Acidity and C.D.	69	148	
Copper	Acid sulphate	40-62	Columnar crystals—large in soft deposits—finer or twinned in harder deposits	H2SO4 conen.	40	102	
	With colloids	Up to 130	Fine fibrous structure	Presence of colloids	***	***	
	Cyanide	130-160	No definite structure			***	
	Neutral nitrate with ammonium	300	No definite structure	******			
Silver	Cyanide	60-79	Not available	Nature of added anion	25*	68*	
Day of	Cyanide with colloid	130	Not available	Presence of colloid			
Cadmium	Cyanide	12-22	Not available		20	(Forged)	
	Cyanide with colloid	53	Fine fibrous structure	Presence of colloid			
Zinc	Sulphate	40-50	Not available		33-40	52	
Tin	Sodium stannate	8-9	Indefinite broken struc- ture — coarse columnar	Temperature	4-5	***	

<sup>\*</sup> R. H. Atkinson and A. R. Raper, Jour. Electro-Depos. Tech. Soc., Vol. 9, 1934, page 77.

such as pH and current density, but without the most careful control of these factors the appearance of bright plate was formerly more often indicative of brittleness and exfoliation than of a desirable condition. Good, ductile, strong and adherent plates then had a "matte" or full velvet appearance. Addition agents, both organic and metallic, now make the production of brilliancy in the bath quite readily controllable, so that thick, bright plates with good physical properties are more common. The advantage of these methods is largely economic, as they yield a reduction in the cost of production of protective high finishes.

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The hardness of a nickel electrodeposit is rather easier to determine than such properties as tensile strength and elongation. Since the relations of hardness to the other properties are reasonably definite,

Table 11.—Properties of Electrodeposited Nickel at High Current
Densities<sup>10</sup>

Ultimate Tensile Strength	Elong.	Hardness Number				
lbe. per sq. in.	Av. %	Brinell .	Vickers			
105,000	7	196	195			
95,000	6	194	186			
88,000	12	171	172			
69,000	25	124				

hardness results give a good general idea of the other properties. Besides this the hardness as such is a useful measure of certain applications of the deposit.

McNaughtan and Hothersall<sup>9</sup> have discussed the hardness of electrodeposited metals and have given an interesting list (Table I) of the hardness of twelve electrodeposited metals. Also Blum and Kasper<sup>10</sup> have given some figures on hardness and other physical properties of deposits made at high current densities. Typical data are given in Table II.

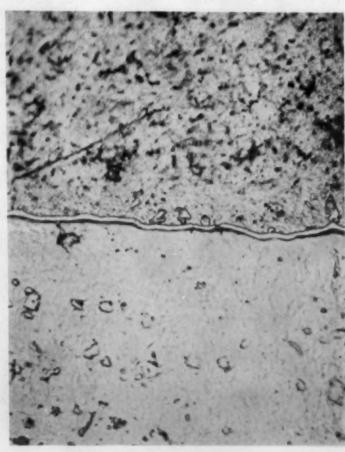
Typical data are given in Table II.

Referring to Table I, the range of hardnesses given for nickel is striking in breadth. While the lowest Brinell number given for the electrodeposits is not as low as the number given for "fully annealed" metal, this is probably due partly to the method of de-

termining the hardness. In the laboratories of the International Nickel Co.<sup>11</sup> it has been found possible to plate nickel as soft as annealed, forged or rolled metal. On the other hand, the greatest hardness is considerably above that which can be produced by cold work. Obviously, nickel electrodeposits should not be considered as restricted in physical properties, but rather as being unusually versatile in form.

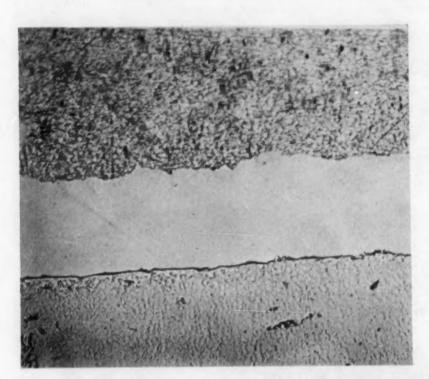
Crystal Structure: The crystal structure naturally varies with the other features of the deposit. The softer deposits tend to be columnar and large grained

An 0.00005 In. Nickel Deposit on Cold Reduced Steel. Magnification 1,000 diameters. The thin nickel deposit, center, above the steel shows some porosity.



and the harder deposits small grained, and in some cases the structure is not resolvable under the microscope. In good deposits no greater porosity is to be seen than with rolled metal. According to McNaughtan's theory the harder and smaller grained deposits are caused by co-deposition of colloidal nickel hydrate and, after annealing such deposits, non-metallic matter is visible at grain boundaries. Typical microstructures of hard and soft deposits show that, like the hardness numbers, crystal size varies in a wider range than in cold worked metal.

An interesting metallurgical phenomenon noted by several investigators is that the grain structure of electrodeposited metals, including nickel, tends to follow and perpetuate the structure of the base on which it is deposited. This has some possible value as an



An 0.0015 In. Nickel Plate over Steel. Magnification 500 diameters. This deposit is sufficiently thick to eliminate such pores as appear in the previous photomicrograph.

investigational method in the study of structures13 but has not yet been used to any practical advantage. Nickel is less susceptible to this peculiarity than are several other metals.

Adherence: While adherence is not properly a property of the electrodeposited metal, some reference to it is necessary. Proper adherence to the ordinary basis metals seems to be largely a matter of preparing a clean and uncontaminated surface for plating. The methods for insuring this vary mainly with the basis metal and its surface condition.

While adherence is difficult to measure, it is possible to plate a sample in such a manner that the electrodeposit cannot be torn away from the basic metal. If proper cleaning and plating procedure has been used, it will be found that separation will occur in the weaker metal, near but not in the bond itself. On the other hand, deposits may be put down so they can be readily separated if and when desired.

Location of the Plate: By control of certain features of the plating, the distribution of the deposit can be controlled within limits. This ability has usually been discussed under the subject of "throwing power," or the ability to throw nickel past a protuberance or into a crevice or niche. High "throwing power" is of value where it is desired to cover uniformly the whole of an uneven surface. On the other hand, in some cases, as in electroforming and in the repair of worn parts by deposition, it is desirable to concentrate the nickel in certain areas. Nickel baths can be made to vary considerably in throwing power. Mainly, the distribution of the deposit is determined by the shape and position of the anodes and the resistance between them and the cathode area. The extent to which nickel varies from "straight line deposition," that is, the distribution determined by the positions of the anode and cathode, can be varied considerably by using baths of varied throwing power. Where it is desired to limit the deposition entirely to definite areas, this is readily done by the use of "stopping off" agents.

Costs: The ability to use various methods of plating and to produce deposits of desired properties tends to lower the plating costs. In general, the methods and raw materials used in obtaining these effects are not inherently expensive. Modern handling methods, including machinery for carrying single items, such as pieces of hardware or sheets, through a bath, and particularly strip plating, where the strips may be handled continuously over rolls, requires only a nominal labor outlay, which is reasonable compared with other handling procedures. Solution losses may be a large item,

but it is usually practical to install simple recovery

systems which lessen this expense considerably, Polishing and finishing costs have been in the past the major expense in producing a brilliant finish. The ability to use bright plating baths in many cases makes a distinct cut in these expenses. Thus, on the whole, it seems that production nickel plating today, considered with respect to the ware or metal plated, should compare roughly with the other cheap fabricating operations such as, for instance, pickling or annealing. The cost of electrodeposited nickel per pound depends somewhat on the thickness and on the conditions of electrodeposition, but this cost also compares favorably with other single processes of metal working.

Note: pH is calculated from and is directly proportional to the observed potential of a hydrogen electrode (solution potential of hydrogen). The symbol really represents the reciprocal of the calculated concentration on a logarithmic scale. This rather complicated relation gives the following useful reference numbers. The only drawback of the system is that being reciprocal, a small pH number represents high concentration or activity; in speaking of high or low values it must always be made clear whether reference is to pH or hydrogen ion concentration.

Calc. g./lit. hydrogen ion 0.1 0.01 0.001 0.0001 0.00001 0.000001 0.0000001

#### References

- <sup>1</sup> M. R. Thompson. Transactions, American Electrochemical Society, Vol. 41, 1922, page 333.

  <sup>2</sup> W. Blum and C. Kasper. Transactions, Faraday Society, Vol. 31, 1935, page 1203.

  <sup>3</sup> D. J. MacNaughtan and A. W. Hothersall. Transactions, Faraday Society, Vol. 24, 1928, page 387.

  <sup>4</sup> D. J. MacNaughtan, G. E. Gardam and R. A. F. Hammond. Transactions, Faraday Society, Vol. 29, 1933, page 729.

  <sup>5</sup> G. B. Hogaboom, Private Communication.

  <sup>6</sup> Tentative Specifications for Electrodeposited Coatings adopted by the American Electroplaters' Society and American Society for Testing Materials, A. S. T. M. Standards, 1935, page 212.

  <sup>7</sup> A. W. Hothersall and W. N. Bradshaw. Journal, Society of Chemical Industry, Vol. 54, 1935, page 320T.

  <sup>8</sup> Strausser, W. C. A. Brenner and W. Blum. Journal of Research, National Bureau of Standards, Vol. 13, 1934, page 519.

  <sup>9</sup> D. J. MacNaughtan and A. W. Hothersall. Transactions, Faraday Society, Vol. 31, 1935, page 1168.

  <sup>10</sup> W. Blum and C. Kasper. Transactions, Faraday Society, Vol. 31, 1935, page 1203.
- Society, Vol. 31, 1935, page 1168.

  W. Blum and C. Kasper. Transactions, Faraday Society, Vol. 31, 1935, page 1203.

  M. A. Wesley. Private communication.

  D. J. MacNaughtan, G. E. Gardam and R. A. F. Hammond. Transactions, Faraday Society, Vol. 29, 1933, page 729.

  A. W. Hothersall. Transactions, Faraday Society, Vol. 31, 1935, 1935. page 1242.

# Corrosion Resistance of Ancient Iron

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By A. W. SIMPSON AND F. N. SPELLER

Department of Metallurgy and Research, National Tube Co., (Subsidiary U. S. Steel Corp.)

THE PUBLICATION of an interesting account of the finding a few years ago of certain implements and pieces of ancient iron in a good state of preservation suggested that a test be made to determine the corrosion resistance of this iron in comparison with that of modern wrought iron and steel. The discovery was made by the Yale University Archeological Expedition organized by the Fine Arts Department of the university in cooperation with the French

Academy of Science.

The site of the discovery was Dura-Europos, an ancient stronghold on the Euphrates River, once held by Alexander the Great and assigned by him to one of his victorious generals. After being held for five centuries by the Romans, it was captured and destroyed in 256 A. D. by the Sassanians. Desert sands drifted over and hid the spot for seventeen centuries until in 1922 a company of British soldiers, in digging trenches along the Euphrates River at this place, uncovered the walls of an early Christian church. However, it was not until 1929 that the Yale Archeological Expedition started its work of exploration on the site. Among the many articles discovered were ancient iron implements, a horse panoply of iron scale armor, and a few loose plates of scale armor.

These articles today form a part of the collection of the Yale Museum of Fine Arts which kindly supplied, for this investigation, several pieces of the scale armor, about 3 in. by 1¾ ins. averaging about 0.022 in. thick; an arrow quarrel, 3 ins. long, and three other severely corroded pieces resembling parts of swords or daggers. Four of the pieces of scale armor were fastened together by small forged copper wires to form a series of overlapping plates. The wires were inserted through four holes, two at each side of a piece of the scale armor. The armor was somewhat rusted but still showed some of the blue forged scaled surface. There was no galvanic attack around the holes through which the copper wires were inserted.

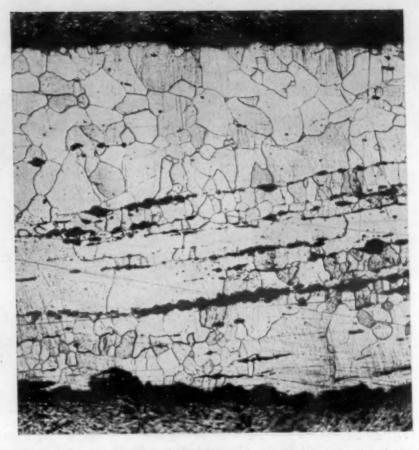


Fig. 1. Section of One of the Armor Scales Showing Ferrite Grains Intermingled with Oxide. This and the next micrograph (Fig. 2) show the full thickness of the armor scale with the edges supported by mounting metal. Magnification, 100 diameters.

The arrow quarrel was slightly rusted and had one deep pit about ½ in. from the point. Its socket, into which a wooden shaft was fitted, was still in good condition. The pieces resembling parts of swords or daggers were so completely rusted that very little metallic iron remained.

The object of the investigation was to determine the comparative corrosion resistance of this ancient iron and the modern ferrous materials, wrought iron and steel.

Fig. 2. Section of Another Armor Scale Showing, in the Lower Half, the Structure of Low Carbon Steel Somewhat Banded. Magnification, 100 diameters.

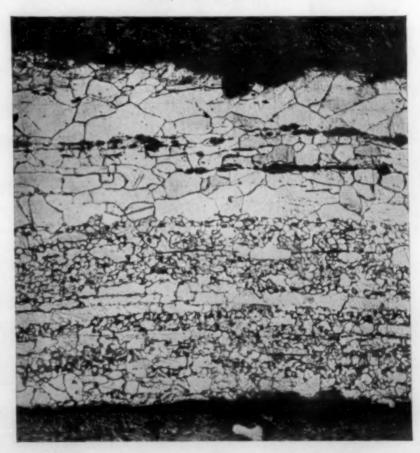




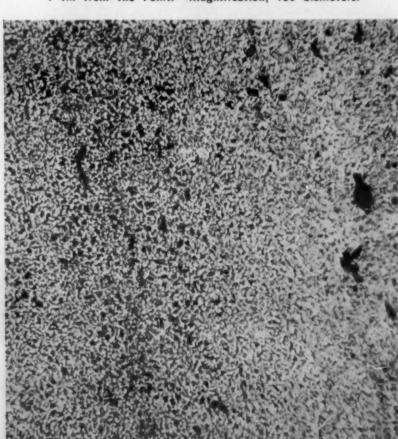
Fig. 3. Section through the Weld at the Bottom of One of the Pieces of Ancient Armor Scale Showing a Sorbitic-Pearlitic Structure of Medium Carbon Steel. Mounting alloy entering the weld is present at lower edge of photograph. Magnification, 100 diameters.

#### The Procedure Adopted

For this purpose, four pieces of the scale armor were selected and two corrosion test specimens, 1 in. by 1¼ in., were sheared from the center of each piece avoiding the punched holes. The clippings from the edges were mixed together to make a composite sample for chemical analysis.

Since the scale armor was somewhat corroded, specimens of modern wrought iron and steel sheet of about the same gage were obtained by shearing previously-used corrosion test pieces from a test conducted at Washington, D. C., by Committee A-5 of the American Society for Testing Materials. Eight specimens,

Fig. 4. A View of the Arrow Quarrel in Transverse Section about 1 In. from the Point. Magnification, 100 diameters.



1 in. by 11/4 in., were obtained from each of the pieces from the previous test.

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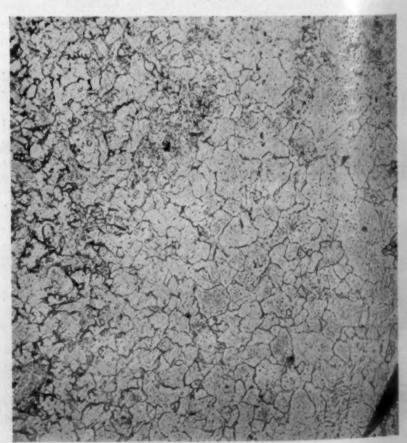
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In order to suspend the test specimens in the corrosive medium, two 0.20-in. diameter holes were drilled near the ends of each specimen. Through these holes, two insulating rods were inserted. Eight specimens of the same material were arranged on a pair of the rods. The specimens were kept ½ in. apart by small insulating spacers on the rods. The corrosion test was run in a 12-liter capacity Pyrex jar.

By means of the rod assembly just described, the specimens were supported in a horizontal position in the corrosive medium held in this jar. The rod assembly was attached to one of eight small spur gears

Fig. 5. A Second View of the Arrow Quarrel at Another Location in the Same Section. Magnification, 100 diameters.



which were mounted on the rotating carriage of the corrosion test apparatus. The small spur gears were spaced equal distances apart on a 5-in. diameter circle. They meshed with a larger stationary gear, centrally located. As the carriage was revolved around the central axis, it caused the rotation of the small spur gears. Thus the specimens suspended from the spur gears were given a planetary motion of translation through the corrosive medium by the carriage and a separate motion of rotation by the small spur gears.

#### The Corrosive Medium Used

The corrosive medium was aerated Pittsburgh city water at a temperature of 160 deg., ±5 deg. F. This water carried about 100 parts per million of dissolved solids. It has a pH of about 6.3, but heating to the temperature of the test drove off some of the free carbon dioxide and reduced the hydrogen-ion concentration, the pH ranging from 6.8 to 7.0 during the test. The aeration was accomplished by means of a glass tube inserted down through the hollow central shaft.

#### Some of the Other Conditions

The other conditions of the test follow:

Volume of solution—8 liters.
Rate of aeration—0.5 cu. ft. of air per hr. measured at 32 deg. F. and 29.92 inches of mercury.

Central shaft speed—3 revolutions per min.

Small spur gear speed—12 revolutions per min. Depth of immersion of the specimens—1.0 in. to 4.8 in.

in seven equal steps. Duration of exposure—3 mos.

Before assembling the specimens on the rods, they were immersed in hot ammoniacal ammonium citrate solution for about 30 min. and subsequently brushed. This treatment removed rust and scale and resulted in a clean fresh metal surface. Before weighing the

specimens, they were placed in the test apparatus and allowed to corrode for two days. After cleaning by brushing only, the specimens were dried and weighed. They were then placed under test for the three months' exposure.

Upon removal from the test, the specimens were cleaned, re-weighed and examined. The examination showed that all but six of the specimens were perforated. Any continuation of exposure to corrosive influences by immersion as reported here or in the atmosphere as planned originally would result in disintegration and loss of the specimens so that the corrosion work on the armor scales was discontinued.

#### What the Analyses Showed

Microscopic examination was made of sections of several of the armor scales, the arrow quarrel, and one of the daggers. In a polished transverse section of the dagger, there was no evidence of metallic iron. Small particles broken from the dagger were only feebly attracted to an ordinary magnet. The amount of metallic iron found by chemical analysis was 1.50 per cent. The full analysis of the dagger follows:

-	-		_	-	- 6	34	9	-	-			_			-				
																			Per Cer
Total iron	 																 	 0	58.50
Metallic iron	 	 																	1.50
ron as FeO	 							0											4.77
ron as Fe2Os																			
ime																			
Magnesia																			
langanese oxide.	 			 															0.09
Phosphoric anhy																			
hlorides	 															0 1	 		0.22
'otal carbon	 										16					0			1.00
Carbon dioxide																			
Sulphur reported																			
gnition loss																			
opper	 							0			 	0	0		0 0				Nil.
Vickel	 										 								Nil.

The analysis of the ancient armor scales, the modern wrought iron, and the steel used in the corrosion test will be found in the table.

#### Table of Analyses of Materials

	C	Mn	S	P	Si	Cu
Dura-Europos *	0.09	0.01	0.007	0.114	0.013	Nil.
Wrought iron	0.03	0.06 to 0.07	0.019 to 0.021	0.153 to 0.160	0.20 to 0.25	0.020 to 0.024
Steel		0.54 to 0.55	0.027 to 0.028	0.006 to 0.008	0.20 to 0.23	0.012 to 0.016
* The Dura-Europos sample wa	s free from Ni a	nd Cr.				

Fig. 6. A Third View of the Arrow Quarrel at Another Location in the Same Section. This view shows the junction lines where these separate particles of metal were united by welding. Magnification, 100 diameters.

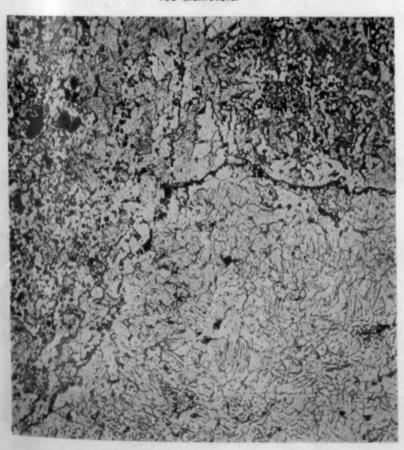
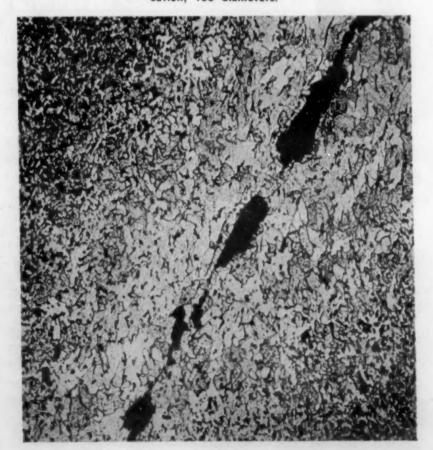


Fig. 7. A Fourth View of the Arrow Quarrel at still Another Location in the Same Section. This view shows large particles of cinder which run diagonally across the section from one corner. Magnification, 100 diameters.



#### Results of Metallographic Examination

The metallographic examination of the armor scales and the arrow quarrel showed considerable heterogeneity of structure. For the most part, the armor scales consisted of ferrite grains intermingled with a substantial amount of oxides as shown in Fig. 1. But structures of low carbon steel were found. These were more or less banded as illustrated in Fig. 2. In both these figures, there are evidences of Stead's brittleness in the enlarged ferrite grains. On one piece of armor scale, there appeared to be a very imperfect weld at the lower end. This is shown in Fig. 3 with an unusual amount of carbon, the structure being fine grained in places like that of normalized medium carbon steel. Along the weld and at the surface, the carbon has been removed by decarbonization. The general structure is sorbitic-pearlitic, a structure which will be caused by rapid cooling in air.

The four other micrographs show the structure of

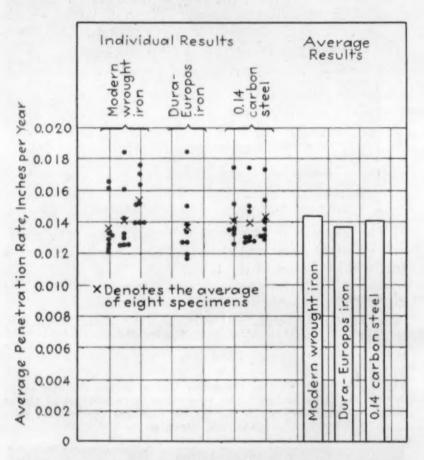


Fig. 8. Corrosion Tests Results Plotted Show no Definite Differences in the Corrodibility of the Ancient Iron and Modern Materials.

the arrow quarrel in a transverse section about 1 in. from the point. They may indicate an intentional selection of pieces resembling medium carbon steel to give rigidity and hardness to the quarrel. The fineness of the grain structure shows that considerable mechanical work was done in forging these pieces to shape. There is also some evidence of reheating. All microsections were etched in a mixture of 5 per cent picric acid and 2 per cent nitric acid in alcohol.

It is significant to note that the structure of this iron is much the same as that of charcoal wrought iron armor made about the year 1500, as illustrated in an article by Prof. William Campbell of Columbia University on "The Structure of Armor, Ancient and Modern," Metals and Alloys, October, 1935. As the period of manufacture of the Dura-Europos iron has been well established by good authority, apparently no material advance in the manufacture or fabrication of wrought iron has been made during this long period of over 1200 years.

The corrosion test results, plotted in Fig. 8, show

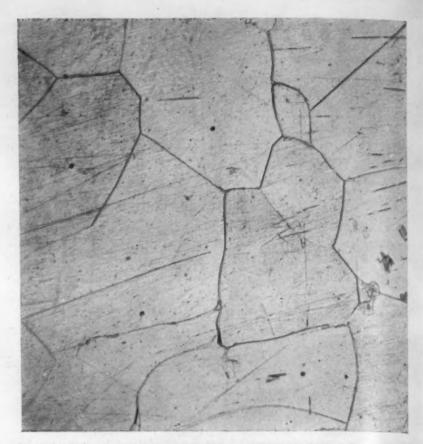


Fig. 9. Egyptian Iron Showing Coarse-Grained Polyhedral Ferrite in Transverse Section and Quite Free from Inclusions. Etched in picric acid. Magnification, 100 diameters.

no definite differences in the corrodibility of the ancient iron and the modern materials. Two of the eight specimens of ancient iron show slightly less corrosion than the modern materials, but the scatter of the points is too great to justify any choice among the three materials under the conditions of test.

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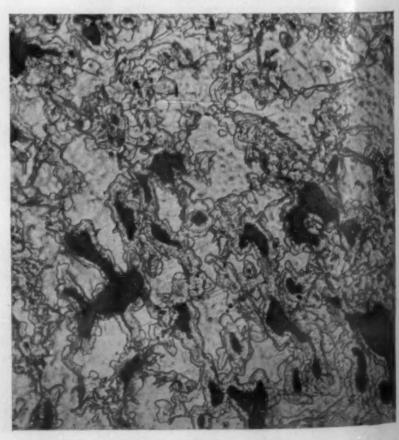
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Sir Robert A. Hadfield, in his introductory remarks to his paper on "Corrosion of Iron and Steel" (Hadfield and Main, Jr. of the Institute of Civil Engineers, England, Session 1935-1936), says in regard to the Delhi Pillar (A.D. 300) that this iron has no different qualities than those possessed by modern wrought iron, and rusted when exposed to laboratory air overnight.

Fig. 10. Another Transverse Section of the Egyptian Iron through the Double-Boundaried Grains with Inclusions of Cinder. Etched in picric acid. Magnification, 100 diameters



#### Some Old Egyptian Iron

Another specimen of ancient iron, from an iron clasp taken from an old Egyptian monument said to be 2,000 years old, was supplied by the late Dr. F. W. Skinner of New York.

This sample had quite variable structure, ranging from coarse-grained polyhedral ferrite (Fig. 9) quite free from inclusions through the double-boundaried grains of Fig. 10 with inclusions of cinder, and that of Fig. 11 in which a coarse grain with phosphorus ghosts is surrounded by fine grains, up to that of Fig. 12 with globular ferrite.

These structures indicate very great irregularity in temperature and degree of working in the hammer forging of the clasp. The micrographs are transverse sections, picric acid etched. This is a very old example of copper-bearing iron. In the picric acid etch, copper plated out upon the specimen.

The Egyptian iron, together with specimens cut from modern wrought iron and open-hearth steel pipes, was compared as to rate of initial rusting. Polished specimens were exposed to water vapor rising from a hot aerated water bath. All three materials tarnished at about the same rate, one corner of the

Egyptian sample being a little darker.

The specimens were re-polished and exposed outdoors at 60 deg. F. in a slight drizzle; all were covered with spotty brown rust in three hours. They were again re-polished and immersed in hot aerated water at 120 deg. F.; all started to rust in 5 min. The Egyptian sample took on a somewhat darker film than the others. After an hour's immersion, the specimens were about equally rusted, and on subsequent exposure to air the quantity of rust appeared to be about the same on all.

This investigation shows once again that ancient iron has no less susceptibility to corrosion than modern ferrous materials and that its preservation at isolated spots on the earth's surface can be reasonably explained by the favorableness of the location. In the present case, the preservation was probably due to the dryness of the atmosphere.

Fig. 11. A Coarse Grain with Phosphorus Ghosts Surrounded by Fine Grains in the Egyptian Iron. Etched in picric acid. Magnification, 100 diameters.



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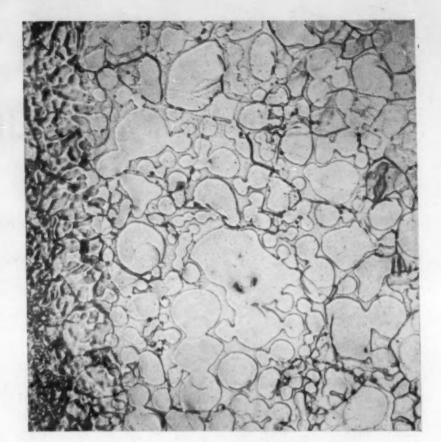


Fig. 12. Globular Ferrite in the Egyptian Iron. Etched in picric acid. Magnification, 100 diameters.

The initial rate of attack under these various conditions of corrosion showed no outstanding difference among the three samples, and the Egyptian sample acted as a modern copper-bearing iron would act.

#### General Conclusions

The very precise tests made in various water solutions reported by G. D. Bengough and F. Wormwell<sup>2</sup> of the Chemical Research Laboratory, Teddington, England, are summed up by these authors as follows:

The general conclusion to be drawn from the experiments on carbon steels of different composition and method of manufacture is that, in the authors' conditions, they all corroded at rates so alike as to be indistinguishable except by refined methods of testing; the principal variations in rate that have been found in the later stages of experiments are to be attributed to secondary effects of corrosion products, and not to the difference between the metals. Changes in external conditions, such as rate of oxygen supply, composition of liquid, and composition of atmosphere, have much greater effects on corrosion rates than any differences between the steels.

Controlled comparative tests of wrought iron and carbon steels made by various processes during the past 20 years, including the extensive tests in water and air by the American Society for Testing Materials and the 12-year soil corrosion investigation of the National Bureau of Standards, point to the same conclusion.

It now seems to be a well-established fact that, under immersed conditions, variations in manufacture, composition, and structure of plain carbon steel and wrought iron do not materially influence the amount or distribution of corrosion. The differences in life of these and other metals in ordinary use under such conditions are evidently controlled by factors external to the metal.

#### References

1 John W. Higgins. The Iron Age, Jan. 10, 1935.

<sup>2</sup> The Design, Interpretation and Uses of Standard Corrosion Tests in Salt Solutions and Industrial Waters." Third Report of the Corrosion Committee, Iron and Steel Institute (British), 1935, page 116.

## A Laboratory Vacuum Casting Furnace

#### By JACK H. SCAFF and EARLE E. SCHUMACHER

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ACUUM FURNACES are especially useful in preparing metals and alloys for research purposes. By vacuum melting and casting, sound ingots of high purity can be produced relatively free from inclusions and, as loss of metal by oxidation is decreased, closer composition control is obtained. Moreover, a degree of refining may result, for in reactions in which a volume increase occurs, the equilibrium shifts to conform with the lower pressure, thus allowing the reactions to proceed nearer to completion. In general, the increase in quality resulting from vacuum melting is manifest in improved working properties and a greater resistance to shock and repeated stresses. The reasons for such improvements, while probably associated with refining and degassing reactions, are not completely understood and as this phase of vacuum melting is receiving increased attention in the laboratory, vacuum furnaces are of utility in investigations of this sort as well as for preparing metals for subsequent study.

Vacuum furnaces for laboratory use consist essentially of a vessel connected to a vacuum pump and containing facilities for melting metals in a crucible or hearth. When desirable, a suitable mold is provided into which molten metal can be poured in vacuum by tilting the entire furnace. Several types of furnaces using either resistance or inductive heating are wellknown. Inductive heating, however, is being increasingly used to simplify construction and to increase the speed of melting. Furthermore, inductive heating permits a reduction in the quantity and temperature of refractories in the furnace, thereby reducing the amount of gas from this source, and enabling lower

pressures to be reached.

Induction type vacuum furnaces may be constructed with the coil either inside or outside the vacuum chamber, and each of these types has certain inherent advantages. Furnaces with the coil inside the vacuum chamber, however, are not generally used with the spark gap type of converter so widely used in metallurgical laboratories in this country, because arcing between the turns of the induction coil occurs more readily in a partial vacuum than at atmospheric pressure, and may puncture the tubing of the coil.

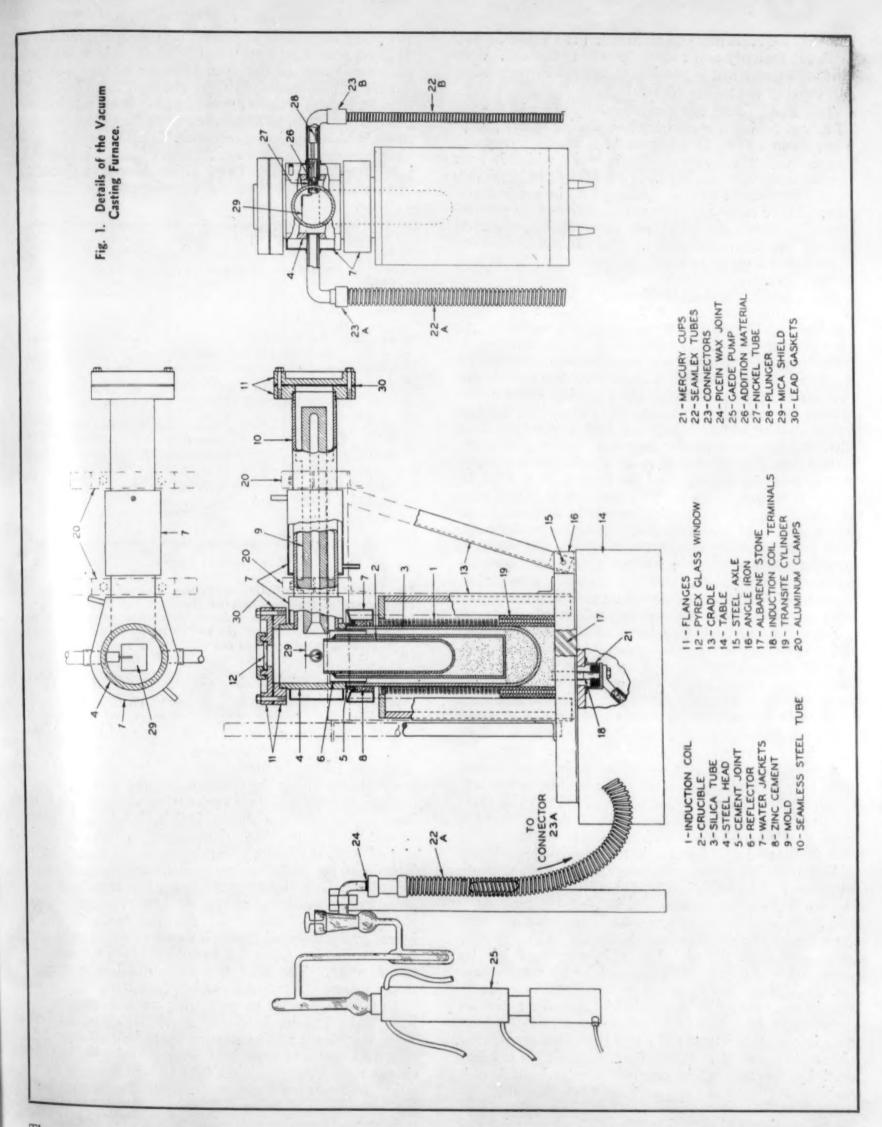
In connection with an investigation at Bell Telephone Laboratories of the effect of certain non-metallic impurities on the properties of metals, a vacuum casting furnace has been developed for use with the standard spark gap type of high frequency converter, in which metals can be melted and cast under pressures as low as 0.01 to 0.08 mm. of Hg. Since this furnace has proved satisfactory for general use in the metallurgical laboratory as well as for studies of the refining and degassing reactions accompanying vacuum melting, the details of its construction and operation are described in this paper.

#### Construction Details and Operation Characteristics

The construction of the furnace is shown in detail in Fig. 1. Two arms at right angles to one another comprise the vacuum chamber, with the induction coil (1) located around the vertical arm. This part of the chamber contains the crucible (2), and consists of a silica tube (3) 5 in. in diameter and 19 in. long, connected to a steel head (4) by a DeKhotinsky cement joint (5). The joint is protected from radiant heat by means of a nickel reflector (6) and from conducted heat by means of water jackets (7) around both the steel head and silica tube. The horizontal part of the chamber is a seamless steel tube (10) and contains the mold (9). It is  $3\frac{1}{2}$  in. in diameter and 22 in, long and is welded and soldered to the head. The openings in the head of the furnace and in the mold tube are fitted with matched flanges (11) and lead gaskets (30). To prevent leakage of gas past the gaskets, two concentric rings, machined on each flange, are forced into the lead by tightening the machine screws which hold the flanges in place. For observing the progress of the melt, the cover flange is provided with a pyrex glass window (12).

The vacuum chamber is supported in a rigid cradle (13) which rests on a small table (14), and is arranged so that it can be tilted from the table through 90 deg. As the furnace and cradle are tilted they are supported by a ½-in. steel axle (15) on bearings welded to angle iron pieces (16), which in turn are fastened rigidly to the supporting table. An Alberene stone base (17) is fitted into the cradle and in addition to supporting the silica tube of the vacuum chamber, it provides the necessary insulation and support for the induction coil terminals (18). A 6-in. high hollow transite cylinder (19), made of 16 rings 3/8 of an inch thick, is fastened to the base. The inside diameter of the assembled cylinder is such that it fits closely around the silica tube and its wall thickness is 1 in. A standard water-cooled induction coil (1) made of flattened copper tubing, is mounted on the top of this cylinder around the central portion of the silica tube. Two split clamps (20) fastened to the cradle by machine screws, support the mold tube (10). To provide an adequate bearing surface each clamp is 11/2 in. wide.

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They are made of aluminum to reduce weight. The silica tube (3) of the vacuum chamber extends into the hollow cylinder (19) to within about 3/4 of an inch of the stone base, and is adequately supported by placing the correct amount of sand in this space. By changing the level of the supporting sand it is also

possible to compensate for slight variations in the lengths of different silica tubes.

Power is supplied to the induction coil by a 35 kva Ajax Northrup high frequency converter. The power leads from the converter are connected to mercury cups (21) fastened to the supporting table. The free

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ends of the induction coil terminals (18) make contact with the mercury and conduct power to the coil. With this arrangement it is possible to tilt the furnace without moving the power leads.

To permit tilting the furnace and yet avoid the use of rubber tubing, the vacuum line leading to the pumping system (22A) is made of "Seamlex" corrugated copper tubing, 1 in. in inside diameter, which is both flexible and vacuum tight. The McLeod gauge line (22B) is made of similar tubing ½ in. in inside diameter. These tubes are soldered, at one end, to connectors (23 A and B) which are fastened into the steel head of the vacuum chamber. The other ends are connected to the glass parts of the system by Picein wax joints (24).

The pumping system consists of a four-stage Gaede mercury diffusion pump (25) backed by a two-stage oil pump. The diffusion pump is connected to the terminals of the flexible exhaust line by glass tubing of 1-in. bore, with a liquid air trap inserted between the diffusion pump and the exhaust line terminal. This provision serves to increase the pumping speed of the system by removing CO<sub>2</sub> and H<sub>2</sub>O from the exhaust gases and in addition prevents mercury vapor from

diffusing into the vacuum chamber.

The crucible (2) is made of a suitable refractory and is 3 in. in diameter, 11 in. long with a 3/16 in. wall. It is usually packed in a larger tube with a suitable heat insulating material, which, in addition to reducing the heat loss sufficiently to prevent the outer tube from reaching a high temperature, also provides support for the crucible itself. Silica crucibles, for instance, are supported in a 3\%-in. silica tube by 36mesh R.R. Alundum, so that the crucible is concentric with the outer tube, with an overall length of 15 in. for the assembly. A thin layer of refractory cement holds the crucible to the top edge of the outer tube. Crucibles assembled in this way require no further preparation after being placed in the furnace and the units can easily be removed on completion of the melt:

Molds for use with the furnace are made of steel. They are designed so that bars 20 in. long by 3/4 of an inch in diameter, and plates 1034 in. long with a cross-section of 21/2 in. by 3/4 of an in. can be cast. Iron bars and plates, cast in these molds, weigh approximately 3 lbs. and 5 lbs. respectively. While these sizes were chosen to suit the needs of the problems at hand, molds of other dimensions may be used.

A feature of this furnace is the provision made for adding materials to the melt at any stage of the vacuum treatment. As shown in Fig. 1, additions (26) weighing up to 20 grams are placed in a nickel tube (27) which fits into the brass tube (23B) and extends over the edge of the crucible. Materials to be added may be pushed from the nickel tube into the crucible by means of a plunger (28) operated by an electromagnet. Additions too large to be handled conveniently by this means may be suspended in the upper part of the crucible from a horizontal rod, one end of which rests in the nickel tube (27) and the other on the far edge of the crucible. When the plunger is moved forward by the magnet it engages the horizontal rod, pushing one end over the crucible edge, and the suspended material drops into the molten metal. Since the supporting rod falls into the melt along with the suspended material, its composition and weight must be such that it will not alter the properties of the final product appreciably. By using this scheme 200-gram additions to the melt have been made.

A mica shield (29) serves to prevent deposition of metal from the vapor phase on the glass window in the cover flange and to protect it from spattered metal. It is supported by a steel rod 1/16 of an inch in diameter connected to the iron cylinder of the plunger. Following the final addition to the melt the mica shield may be removed from the field of view, by moving the plunger forward, to allow measurement of the temperature with an optical pyrometer.

In arranging for a melt, the top edge of the crucible is adjusted by means of crystalline Alundum placed in the bottom of the vacuum chamber, to be approxi-

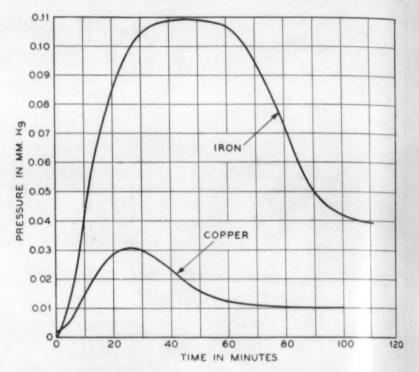


Fig. 2. Pressure-Time Curves for Vacuum Melts of Iron and Copper. For that part of the curve between the origin and the maximum the temperature of the metal is rising to the melting point. From this point on, the temperature of the molten metal is kept constant at 1600 deg. C. for iron and 1150 deg. C. for copper.

mately 1/4 of an inch below the center line of the mold. After the nickel reflector is inserted the charge is placed in the crucible, the furnace closed, evacuated, and the high frequency current is passed through the coil. After the metal has been molten for the required time, the power is turned off and the metal cast into the mold by tilting the furnace through 90 deg.

Typical pressure-time curves for vacuum melts of iron and copper are shown in Fig. 2. These curves show that the pressure rises rapidly as the metal is heated until it reaches a maximum as the metal melts. Then with the metal molten and the temperature maintained constant, the pressure gradually falls to a constant value somewhat above the low pressure obtainable with the furnace cold. This difference in equilibrium gas pressure is probably due to the steady evolution of gases from the heated refractory parts of the furnace. The final pressures obtained are relatively low for a vacuum casting furnace.

In the early work on preparing vacuum castings of iron, disks 23/4 in. in diameter and 1/16 of an inch thick were used as the starting material and considerable difficulty was experienced from "bridging" of the charge across the crucible. The difficulties were overcome, however, by using an iron cylinder as the starting material, cut from a 21/2 in. rod to the correct weight, and by using a crucible with an inside diameter sufficiently large to give 1/8 to 1/4 of an inch clearance around the metal charge. No "bridging" difficulties of any kind have been experienced with other materials. Iron-nickel alloys, copper alloys, and other materials are prepared using starting materials in a wide variety

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### THE FE-CR ALLOY SYSTEM

#### The Brittle, Non-magnetic Phase

By ERIC R. JETTE and FRANK FOOTE

Associate Professor and Research Assistant in Metallurgy, Columbia University, New York

Wo IMPORTANT PAPERS on the constitution of the iron-chromium alloys appeared in 1931. Wever and Jellinghaus¹ reported the existence of a new phase in the neighborhood of the composition FeCr. Adcock², in spite of certain specific experiments for the purpose, was able to find nothing but the body centered cubic alpha phase. Adcock's alloys were probably the purest alloys of this system ever produced while those of the German authors left something to be desired in this respect. Greaves³, reviewing all the experimental work prior to January, 1934, which concerned this compound, surmised that some impurities in the alloys of Wever and Jellinghaus were responsible for the effects observed.

Later Eriksson<sup>4</sup> reinvestigated a portion of the Fe-Cr system apparently in ignorance of the X-ray work performed by Preston<sup>5</sup> on Adcock's alloys. These alloys were possibly not quite as pure as Adcock's although the article gives no definite information on this point. The X-ray evidence of the existence of a new phase occurring over a considerable range of compositions was unmistakable. Eriksson did not find it possible to establish its homogeneity limits. The diffraction pattern indicates that the structure of this

phase is very complicated.

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In the meantime an extensive investigation of the iron-chromium-silicon phase diagram by X-ray methods was in progress in this laboratory. A compound was found over a wide range of compositions which gave X-ray diffraction patterns qualitatively similar to those reproduced in the article by Wever and Jellinghaus. Further exploration showed that, under the proper conditions of heat treatment, these same diffraction patterns were obtained, at progressively lower silicon contents, along the line in the ternary diagram where the ratio of atom per cent chromium to atom per cent iron was unity; the last alloy contained only 0.087 per cent wt. % Si. The diffraction pattern of this phase is strikingly different from that of the alpha-iron phase; it also bears no resemblance to any known nitride, carbide, or oxide of iron or chromium. There seemed to be no doubt that the phase occurring inside the ternary diagram was the same as that at the binary limit.

The present article is based partly upon observations made in the above mentioned investigation of the ternary diagram and partly upon new work on some binary alloys of high purity. It is an attempt to establish whether or not the compound exists in binary alloys of high purity and to account, at least in part, for the discrepancies between the previous investigations. The new phase will be called the sigma phase in this article. It should be observed that it is non-

magnetic and very brittle.

#### Preparation of the Alloys

Carbonyl iron and a specially purified electrolytic chromium were used. More complete analyses of these metals will be given in the article on the ternary

system.

Alloys Nos. 3 and 4 were made by melting weighed quantities of the metals in an alundum crucible lined with pure fused Al<sub>2</sub>O<sub>3</sub> using a suitable distribution of 120 mesh with finer material and a concentrated AlCl<sub>3</sub> solution for a binder. The crucibles were fired in a graphite container by a high frequency furnace and later in a muffle at 1000 deg. to remove adhering graphite. The alloys were melted in vacuo after flushing out the system several times with hydrogen. They were allowed to cool in vacuo. A slight amount of oxidation always took place. Alloy No. 71 was prepared during the investigation of the ternary system. Aside from the fact that it was made in an unlined Norton alundum crucible, its preparation and heat treatment in the ingot state was identical with the others.

Carbon contents on a number of ternary alloys made under these conditions have never been greater than 0.02 per cent. Silicon and iron contents are reported in Table I. The reason for the importance of the silicon content will be given in the discussion.

#### Table I.—Analyses of Iron-Chromium Alloys

Alloy No.	Wt. % Si	Wt. % insol.*	Wt. % Fe	At % Fe	Lattice Constants
3	0.006**	0.90	50.3	48.5	
4	0.003	0.55	52.4	50.6	2.8692
71	0.086		51.48	49.70	2.8693

\* X-ray analysis showed that the residue was practically all Cr2Os. \*\* Single determination by F. Foote.

The ingots were annealed in hydrogen for one week at approximately 1000 deg. C. to eliminate any coring or other inhomogeneity. Slight oxidation occurred during this anneal; the surface was cleaned by grinding. Fine chips made by a milling machine were secured from alloys Nos. 3 and 4. These chips were sealed up in small, throughly cleaned and evacuated quartz tubes. They were then annealed for 5 days at approximately 700 deg C. which converted them almost completely to the sigma phase form. Grinding in an agate mortar to pass through a 200 mesh sieve was thus made possible. After grinding, portions of the sample were sealed in evacuated quartz tubes. One portion was annealed again at 700 deg C., if it was necessary to complete its conversion to sigma. Another was heated at 1000 deg. C. for 5 hrs. to transform it back to the alpha form. The sample at 1000 deg. C. sintered somewhat and was broken up by careful tapping and rubbing in an agate mortar. A certain amount of cold work was thus given this portion of the sample which later proved to be of considerable importance. Subsequent operations are indicated in Table II. Alloy No. 71 was made into a powder by careful grinding of the annealed ingot with a small alundum wheel. These grindings were put through a 100 mesh sieve and, after sealing in evacuated quartz tubes, were annealed as stated in Table II.

Table II.—Annealing Treatments of Fe-Cr Alloys

Alloy No.	Phases present before anneal	Temp., deg. C.	Time,	Test with magnet	Phases present in X-ray films
3 4 4 4 4 4 71 71	mostly Σ  α Σ α Σ α (Σ?) α (Σ?) α (Σ?)	1049 904 904 800 800 775 775 767 773 775	18 18 22 22 24 44 44 3 16 86	magnetic magnetic magnetic magnetic slightly magnetic partly magnetic non-magnetic	all $\alpha$ all $\alpha$ all $\alpha$ all $\alpha$ all $\alpha$ some $\alpha$ mostly $\Sigma$ $\alpha + \Sigma$ all $\Sigma$ all $\alpha$ mostly $\alpha$ some $\Sigma$ more $\Sigma$ than No.
4 4 3 3 3 4	a (Σ?)  a Σ mostly Σ a a a	756 756 717 716 710 600	44 44 141 37 161 48	non-magnetic non-magnetic partly magnetic slightly magnetic non-magnetic non-magnetic	71, 16 hrs. Σ only Σ only α but mostly Σ trace α all Σ Σ only

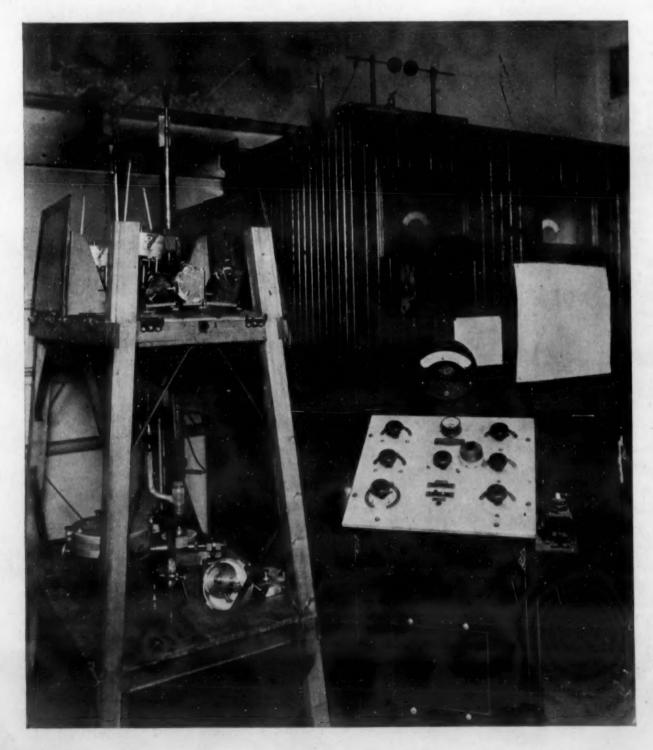
Since this investigation was primarily intended to identify the phases present in the system, it was unnecessary to make a complete set of lattice parameter measurements. Aside from the fact that focusing cameras of the Phragmén type were used with chro-

mium radiation, the details of the X-ray work are unimportant here. It may be mentioned, however, that in every case (eight in all) where the lattice constants of binary Fe-Cr alloys have been measured in this laboratory, the differences between our results and those of Preston are well under 0.001A.

#### Discussion of Results

The fact (1) that this sigma phase existed over a wide range of compositions in the ternary iron-chromium-silicon system, and (2) that Adcock's alloys were very low in silicon, at first suggested that the silicon might be responsible for the difference between the latter's results and our own; if true, this would also explain the difference with respect to the results of Wever and Jellinghaus. The silicon contents of Eriksson's alloys are not known. Alloy No. 71 contains less than two atoms of silicon per thousand while alloys No. 3 and No. 4 contain less than one-tenth this amount.

It would at first sight seem highly improbable that such small concentrations of silicon could actually give rise to the existence of a phase which did not occur in the pure binary system. While such a case would yield a ternary equilibrium diagram of most unusual appearance, it is in fact not justifiable to dismiss this possibility entirely. It is well known that in certain binary



X-Ray Apparatus in the Laboratory of the School of Mines, Columbia University.

systems a new phase does not occur at precisely the composition of the simplest formula corresponding to the crystal structure. Instead, it is found somewhat to one side of this simplest composition and in this same direction may have a more or less extensive homogeneity range. Such cases have been found in the iron-silicon system<sup>7</sup> at the compound FeSi<sub>2</sub>; in the copper-tin system8 at CuSn; in the Fe-O system9 at the compound FeO; and also in the Ni-Sn system<sup>10</sup>.

Westgren and his co-workers have usually interpreted this to mean that a certain excess of one of the elements apparently was necessary to "stabilize" the lattice. Any satisfactory theoretical reason why such a situation should exist seems lacking at present although the method of attack used by H. Jones<sup>11</sup> in his work on the typical γ- and ε-structures may well yield important information. Since the lattice as a whole changes in size with the composition, one might perhaps hazard the guess that certain maximum or minimum average interatomic distances are not stable and the presence of small amounts of one of the elements brings this average interatomic distance within a range of stability. Regardless, however, of what the real reasons for such a stabilizing effect may be, it seems obvious that some third element may serve quite as well as one of the constituents of a binary compound. What this may do to our present conceptions of "pure (?) binary equilibrium diagrams" is, unfortunately, quite obvious, and in more pessimistic moments the investigator may wonder if a very high "purity" of materials is really useful.

A second possibility is that the sigma structure actually is stable in the pure binary system but that the very slow transformation from alpha to sigma or vice versa is accelerated by silicon. There have been a few qualitative observations during the course of the investigation of the ternary system which indicated that silicon did have such an effect on the transformation in both directions, particularly in the ingot form. Unpublished results by Andersen and Jette<sup>12</sup> are of interest in this connection. Alloy No. 71 in ingot form showed considerable areas of sigma phase after 18 hrs. at 1025 deg. C. and apparently little change in the relative amounts of sigma and alpha phases after heat treatment for 59 hrs. between 725 deg. and 750 deg. C. The Brinell hardness after quenching from 1025 deg. was 245; after 41 hrs. at 750 deg. 255; after a further heating at 725 deg. for 18 hrs. 250. Microscopic examination of a second sample of the same alloy heated for 96 hrs. at 730 deg. C. showed that precipitation had started but had not progressed very far; the Brinell hardness was 255. Another alloy with 1.8 per cent silicon (51.4 wt. % Fe) was almost entirely convented to alpha with a Brinell hardness of 245 by the treatment at 1025 deg. and after 41 hrs. at 750 deg. was so completely converted to sigma phase that it was too brittle for a hardness test. The mechanism of the effect of silicon is quite obscure. For various reasons the term "catalytic effect" is unsuitable, so that for the present it seems best to be content with the simple statement that silicon does increase the rate of transformation.

A third and apparently even more important influence on the rate of transformation is cold work or mechanical distortion of any kind. The work of Mooradian and Norton 13 has indicated that lattice distortion is not an aid to diffusion. The present problem, however, involves a process which is comparable to a polymorphic transformation and in this particular case diffusion is probably of minor importance since both phases have the same composition. (It is obvious that if the process is alpha → alpha+sigma, i.e., the equilibrium point for a specified temperature and composition lies in a two-phase region, this statement will not be true and we would resort to other principles of heterogeneous reaction rates). atomic displacements are probably small.

The experiments reported in Table III were per-

Table III.—Special annealing experiments at 600 deg. C. with strain relieved alpha-phase alloys.

			remered aipina	pilase alloys.	
Exp.	Sam- ple No.	Anneal Time, hrs.	Magnet Test	Phases on X-ray Film	Remarks
1 2 3	4A-I 4A-I 4A-I	133 252 40	strongly mag. strongly mag. separated into mag. & non-mag. parts; mostly $\Sigma$	α trace Σ little α	continuation of No. 1 powder after No. 1 rubbed in mortar
4 5 6	4A-II 4A-III 4A-III	113 278 20	strongly mag. strongly mag. strongly mag.	α trace Σ	continuation of No. 4 sample after No. 4
7	4A-III	45	separable into mag. & non- mag. parts;		very lightly rubbed continuation of No. 6
8	4A-III	69	mostly a ditto, but more $\Sigma$ than No. 7		continuation of No. 7
9	4A-III	165	ditto, but mostly Σ	mostly $\Sigma$	continuation of No. 8
10	4A-IV	4	strongly mag. no mag. sepa- ration		sample after No. 4 given severe rubbing
11 12	4A-IV 4A-V	20	non-mag, strongly mag, mag, separa- tion impossi- ble		continuation of No. 10 sample after No. 4 given severe rubbing

formed with the object of discovering how important an effect cold work might have. Portions of alloy No. 4, which had been treated as described in an earlier section, were given an additional vacuum anneal of ½ hr. at 1000 deg. C. in order to remove the cold work originally present but without seriously sintering the material. The samples marked 4A-I and 4A-II were different lots from the original alloy No. 4 treated at different times. The total annealing time is tabulated. The magnetic tests were made while the samples were sealed inside the glass annealing tubes using a powerful cobalt steel magnet. By careful manipulation it was possible to secure very good separation of the magnetic from the non-magnetic material. This procedure is obviously inadequate to test for initial stages of the transformation since a particle continues to be attracted by a magnet until it is very largely sigma phase. Separation tests were made only in experiments 3 and 6 to 11 inclusive.

Table III shows very clearly that the strain free alloys remain almost indefinitely in the alpha-phase form at 600 deg. C. It also shows that the more severe the degree of cold work, the more rapid the transformation. In experiment No. 9 on a lightly rubbed (in an agate mortar) sample, the transformation was still incomplete after a week at 600 deg. while experiment No. 11 shows that a severely worked sample transforms completely in 20 hrs. or less. Experiments Nos. 2 and 5 show that if the sample was not cold worked, there is scarcely any transformation even after 11 days of annealing at this temperature. It is worth noting that in experiment No. 12, although a considerable amount of sigma phase was present, the blurred appearance of the alpha phase lines indicated that the cold work had not been entirely removed

after 3 hrs. of annealing.

Adcock<sup>14</sup> shows a photograph of an alloy of approximately 50 atomic per cent chromium after annealing 4 days at 600 deg. C. which he believes indicates nothing more than a small amount of recrystallization of the alpha phase, A quotation regarding the microscopic observations on the nature and occurrence of this sigma phase from the above mentioned unpublished work by Andersen and Jette follows: "The sigma phase exists in a large variety of forms in these (ternary) alloys. In some cases, it occurs in well defined massive lumps surrounded by the alpha phase. In others it appears much like martensite<sup>15</sup>. A number of intermediate forms including nodular ones and an apparently finely laminated one have also been observed. In some cases it collects at the grain boundaries. We also have observed this phase uniformly distributed within the grains with no detectable precipitation at the grain boundaries16". The multiplicity of forms in which this phase may exist makes it a treacherous one to investigate by microscopic methods. Even after considerable experience the writers could be misled by some apparently new form which would be interpreted as another new phase until X-ray evidence proved otherwise.

It will be evident from a comparison of the analyses of the alloys that there is not sufficient difference in the compositions to account for the difference between our results and those of Adcock on the basis either of the stabilization of the sigma phase by very small amounts of silicon or of the accelerating effect of the

silicon on the rate of transformation.

The major reason for the difference, therefore, must be ascribed to differences in the mechanical treatments of the alloys leading to different degrees of deformation and to differences in the time of heat treatment. In a personal communication to the present authors, Adcock has very kindly given us the heat treatment of his 48.8 and 50.5 atomic per cent chromium alloys in somewhat greater detail than in his original paper. After a vacuum anneal at 1300 to 1350 deg. C. for 12 hrs. to remove "coring," pieces were vacuum annealed for 4 days at 600 deg. C. "Filings from these alloys were vacuum annealed 30 min, at 600 deg. C. to remove the effect of cold work."

Our results on annealed ingots reported above indicates that a thoroughly homogenized and strain-free ingot would be little affected, perhaps not at all, by 4 days heat treatment at 600 deg C. Table III indicates that 30 min. annealing of the filings would barely start the precipitation. Thus Adcock's results were what would be expected in the light of the present in-

vestigation.

Our results lead to two very definite conclusions: (1) The rate of transformation is increased by sili-

(2) The rate of transformation is increased by cold working the sample.

Regarding the result of Adcock's microscopic examination of the 600 deg. C. ingot referred to above, if we assume his interpretation of the appearance of this sample to be correct, it will readily be appreciated that the alloy remained in the alpha form for a most unusual reason, namely, his alloy was too pure and too well annealed prior to this heat treatment for the transformation to take place in the allotted time.

#### The Transformation Temperature

It is evident from the method of preparing the samples before the final anneal as well as from the results in Table II that the transformation

Alpha ≒ sigma

is a strictly reversible one. The work of Eriksson and Wever and Jellinghaus as well as our own indicates that the sigma phase, even in the binary system, is a secondary solid solution (in the Hume-Rothery

nomenclature). The maximum temperature at which this phase is stable probably occurs at or near 50 atomic per cent. This would be an invariant point and on either side of the homogeneous sigma region below the maximum temperature would be a twophase region. The results in Table II show that for alloy No. 4 with 50.6 atomic per cent iron the reaction reverses direction between 775 and 800 deg. C. The transformation temperature probably lies within these limits, which are considerably lower than the limit of 925 deg. C. given by Wever and Jellinghaus. establishment of the homogeneity range of the sigma phase and the bordering two phase regions will be matters of considerable difficulty, as Eriksson has already pointed out, and time has not permitted this to be undertaken.

#### Summary

PHASE of very complicated structure, the sigma phase, has been found to exist in the neighborhood of the composition FeCr in binary alloys of a high degree of purity. This confirms the earlier results of Eriksson and of Wever and Jellinghaus but

is at variance with those of Adcock. Three factors which can influence the transforma-

tion rate are discussed in the light of the present experimental results: (1) A possible stabilizing effect of silicon on the sigma-phase, which would imply that this phase does not exist in the absence of silicon or some other element with similar influence; (2) an accelerating effect by silicon; and (3) an accelerating effect produced by cold work.

Experimental evidence is given to show that both (2) and (3) are important factors in the ternary Fe-Cr-Si alloys but it is concluded that the difference between the present results and those of Adcock on the binary system are due mostly to the third factor.

The transformation temperature of an alloy of 50.6 atomic per cent Fe is between 775 and 800 deg. C. and the transformation is a strictly reversible phenomenon. The true transformation temperature prob-

ably lies within these limits.

We take this opportunity of expressing our thanks to the Union Carbide and Carbon Research Laboratories for supplying the electrolytic chromium, making the chemical analyses of the alloys, and other cooperation in this work; and to A.G.H. Andersen for reading the original manuscript and clarifying a number of important points.

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# BERYLLIUM AND ITS ALLOYS—II

A Correlated Abstract
By JACK DELMONTE, Sc. M.

East Lansdowne, Pa.

Continued from the July issue

HE future of beryllium lies in its application as an alloying medium. Marked improvements in metals and alloys have been effected by the addition of small amounts of beryllium. The most outstanding examples are the beryllium-copper alloys, whereby small quantities of beryllium effect a unique combination of electrical and mechanical properties. It will be recalled that 90 per cent of the commercial production of the metal in the United States in 1933, went into the production of this class of alloys6. It is beginning to appear as though beryllium holds the same degree of significance to copper as carbon does to iron. Pure copper has low strength and a low resistance to deformation, both of which are vastly improved by the addition of beryllium, to an extent hitherto unattainable in other copper alloys.

Before proceeding with the discussion of the physical properties of the alloys, the constitutional diagram of beryllium-copper alloys facilitates a fundamental understanding of the major beryllium alloys. A critical study by H. Borchers<sup>40</sup> gave the results illustrated in Fig. 4. He reviewed the previous work in this field and introduced his own results. Masing of the Siemens-Konzern likewise has devoted considerable time to the beryllium-copper constitutional diagram<sup>13</sup>. There has been some question as to the accurate shape of the  $\beta$  + liquid region on the diagram, and consequently this region is illustrated in dotted lines. The γ-phase represents a solid solution of beryllium in a phase copper;  $\beta$  is the high temperature phase which decomposes at 580 deg. C. to  $a + \gamma$ . The age-hardening or precipitation-hardening that is characteristic of beryllium-copper alloys has been attributed to the decomposition of the super-saturated solution of the second phase into the  $a + \gamma$  region; not dissimilar to aluminum-zinc, or iron-carbon systems<sup>41</sup>. During the age-hardening at 350 deg. C., the super-saturated a solid solution of 2.0 to 2.5 per cent beryllium-copper alloys has been studied by Dahl, Hohn and Masing, and the appearance of γ-crystals detected by X-ray investigations<sup>13</sup>. Age-hardening of wires which are drawn after quenching takes place in a strongly accelerated manner.

#### Production of Beryllium Alloys

As in the production of pure beryllium, electrolytic methods predominate in the production of beryllium

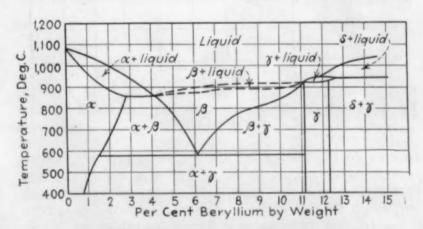


Fig. 4. Copper-Beryllium Constitutional Diagram.

alloys, though a direct addition of beryllium to the base metal is observed to some degree. Electrolytic methods that lead to a direct yield of the alloy are favored over the direct addition, as some have found this latter step meant a greater loss of beryllium than with the electrolytic method. It is likely that the latter method is favored in the United States as

the beryllium yield is in the form of scales and spangles, and it is simple to reheat the yield with some base metal to form a rich alloy. Sloman points out the advantages of using a molten cathode of the metal to which beryllium is to be alloyed<sup>42</sup>, at the same time following the usual electrolytic procedure of beryllium production. The cathode that is obtained in this manner is usually low in beryllium content. Research investigators of Germany note that with a molten cathode of the base metal there are high slagging losses of beryllium.

It has been possible to produce beryllium-aluminum alloys from a melt containing aluminum and beryllium fluorides. The electrolysis takes place at 1200 to 1300 deg. C., and 1 to 40 per cent of aluminum in beryllium has been obtained. The alloy is remelted to get rid of the slag<sup>13</sup>, a difficulty that is always present with the electrolytic methods. Aluminum and beryllium mix in all proportions in the liquid phase, and the fact that the decomposing temperatures of beryllium and aluminum salts are in close proximity, permits this method of production.

Alloys of beryllium with copper and other heavy metals are produced electrolytically by adding the finely divided alloying metal to a fused beryllium oxyfluoride bath<sup>43</sup>. This method is designed to incur a low slag loss of beryllium. The added metal, on

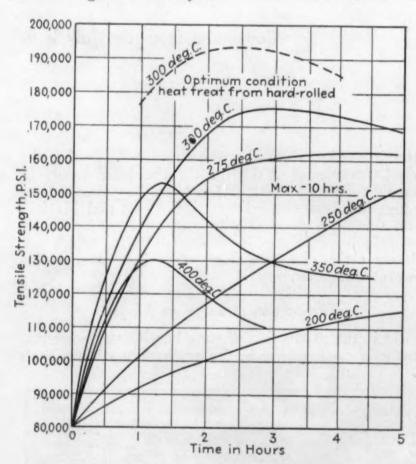


Fig. 5. Effect of Heat Treatment on Soft Annealed 2 Per Cent Beryllium-Copper.

sinking to the bottom of the graphite crucible, which serves as an anode, is converted into a fluoride and is dissolved in the bath. It migrates finally with beryllium to the cathode, where the alloy separates out. In this fashion rich beryllium alloys of heavy metals are secured in Germany. Necessary proportions are added to the base metal to secure an alloy of the specified beryllium content.

In the United States the direct addition of beryllium to the alloying metal is favored. As beryllium is a strong de-oxidizer, before adding it to the copper bath, for example, the bath is treated with boroncarbide, calcium, lithium, or magnesium to rid it of

the excess oxygen. In this fashion as little of the beryllium as possible is wasted. The copper bath is heated to 1200 deg. C. and small amounts of beryllium are added. The bath is not stirred rapidly and hence the absorption of gases is reduced. The pouring temperature, 1040 to 1090 deg. C., is dependent upon the beryllium content. The alloy is cast in ingots if further heat treatment or fabricating is necessary, or castings if required<sup>45</sup>. To place the beryllium-copper alloy in its softest condition, it is annealed at 780 to 815 deg. C. for one hour, and quenched in cold water.

A still further method of producing beryllium alloys may be briefly mentioned at this point, not so much for the success it has shown, as for the fact that it has possibilities. Beryllium chloride vapor is reduced to the metal, on passing into a receptacle containing aluminum. The aluminum chloride and some unreduced beryllium chloride escape. The reduced metal alloys with the aluminum on applying more heat. The yield of the reduced metal is controlled by adjusting the conditions of temperature and pressure<sup>44</sup>.

#### **Electroplating Beryllium**

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High temperature methods permit the best opportunities for the electro-deposition of beryllium18. While maintaining a bath temperature of sodium fluoride and beryllium oxy-fluoride at 700 to 800 deg. C., it is possible to coat a copper sheet serving as a cathode, with beryllium. Considerable hardness is imparted to a copper sheet treated in this fashion. A bath temperature of 550 to 580 deg. C. is recommended for electroplating beryllium on aluminum; and 900 deg. C. for a deposit on iron or nickel<sup>13</sup>. Subsequent heat treatment may produce a superficial alloy of beryllium with the underlying casting, with beneficial results, as the surface will exhibit characteristics of the alloys. It has already been pointed out that beryllium may not be electro-deposited from aqueous solution.

#### Beryllium-Copper Alloys

The unusual properties of beryllium-copper alloys have led to a number of successful applications which hold great promise for the future of the metal. In order to arrive at the desired strength and hardness, or electrical property, a meticulous study of the processing of the alloy is necessary, for marked changes are effected by subsequent working and heat treatment. One of the outstanding advantages of these alloys is the fact that articles may be shaped and machined in the soft condition, and then heat treated to strengths and hardnesses, far beyond those of the present hard bronzes.

Of particular interest is the functional relation of tensile strength and hardness of the beryllium-copper alloys to the duration of heat treatment. Fig. 5 emphasizes the dependence upon the heat treatment, in order to attain any desired physical properties. The curves are drawn after data from several reliable sources<sup>45</sup>, <sup>46</sup>, <sup>47</sup>. It has been pointed out that the peaks in the curves may be arrived at a little sooner than indicated in Fig. 5, by maintaining the alloy in a bath of molten salts at the required temperature<sup>45</sup>, instead of the furnace heat treatment. It will be noted that the referred to curves are for heat treatment from the annealed state. Similar heat treatment of the alloys after they have been hard-rolled,

vield greater values of tensile strength. While it may be possible to secure greater strength by heat treating at 250 deg. C.46, a heat treatment of 300 deg. C. is more to be desired, as the alloy is ready in a reasonable length of time. The heat treatment of heavily cold-worked material is reported to be easier and safer if maintained at 250 deg. C.47. Elongation, for the majority of these fabrication procedures, decreases as the hardness and the tensile strength increase. As far as the other properties as the endurance limit, stability, electrical, thermal, etc., are concerned, they are not necessarily in agreement with the trend of strength during heat treatment. The heat treatment of the berylliumcopper alloys must therefore be selected with reference to the most important properties needed.

#### Wrought Beryllium-Copper Alloys

Beryllium-copper alloys of 1.5 to 4 per cent beryllium content, exhibit the best response to heat treatment. Alloys with a higher content of beryllium are very hard and brittle, making it very difficult to work the metal. An alloy of 6 per cent beryllium, for example, has exhibited a hardness of 730 Brinell; but, on the other hand, it is not possible to produce it in a practicable form because it is unworkable<sup>15</sup>. The wrought beryllium-copper alloys to which have been attributed the greatest possibilities are those with 2.0 to 2.50 per cent beryllium content. The physical properties of this group of alloys are given in Table 3. The data have been compiled

physical properties, as Table 4 indicates, thought not to the extent of the heat treatment<sup>50</sup>.

#### Table 4.-Effect of Rolling Beryllium-Copper Alloys

	Brinell Hardness	Tensile Strength, p.s.i.
Soft annealed	80	54,400
Rolled 2 Nos. hard (20%	red.) 130	86,000
Rolled 6 Nos. hard (50%	red.) 212	108,600

Up to 2.5 to 2.75 per cent Be content, the alloys are cold-rolled, and beyond that, they are usually hot-rolled<sup>18</sup>.

It is no wonder then, that comments on beryllium-copper alloys are very favorable in the technical literature, such as "5 times the tensile strength and 6 times the hardness of copper" beryllium-bronze may be substituted with advantage in all cases where aluminum-bronze or phosphor bronze are used" applicable, where drawable materials of great hardness and high elongation are desired" etc. But what is more important is the fact that the alloys may be machined and fabricated without difficulty. It has already been produced in the form of wire, sheet, tubing, strip, rod, and bars. Beryllium-copper alloys are offered in gages in which phosphor bronze is ordinarily available. 18

Beryllium-copper alloys of 1.5 to 4 per cent beryllium show a marked degree of age-hardening after quenching in oil or water from 750 to 800 deg. C., and followed by artificial aging at 250 to 300 deg. C. Work-hardening following annealing at 800 deg. C., and reheat-treating can further improve the properties, as reference to Table 3 (State D) indicates. Attention is called once again to Fig. 5 to emphasize

Table 3.—Physical Properties of Wrought Bervllium-Copper Alloys

1 abic	J. I lly sical	rioperties of	AA LORPING	perymani-cop	per Alloys			
	State	"A"	Stat	e "B"	State	"C"	State "D"	
Property  Yield point, p.s.i.  Tensile strength, p.s.i.  Elongation in 2 in., per cent.  Young's mod. of elas., p.s.i. × 10 <sup>-6</sup> Brinell  Impact strength, ft. lbs  Elec. conductivity, % of IACS.	88,000 25 16.8 105	U. S. 31,000 80,000 45 18.0 110 59.7	Germany 88,700 123,500 11 18.8 365	U. S. 134,000 175,000 6.3 18.9 340 7.3 (18 to 25)	Germany 111,000 115,000 0.75 265	U. S. 105,000 118,000 4.5 17.2 220 16.7 17.0	Germany 152,000 175,000 5.7 380	U. S. 138,000 193,000 2.0 18.4 365 6.1
Thermal conductivity, % of Cu	30.3	21.2	42	26.5				***
Composition			. 2	.5% Be-Cu	any		United Sta .25% Be-Cu 0.50% Ni	ites
Source of Data State "A" State "B" State "C" State "D" Quenching temperature			S	deference 48 loft annealed empered from Hard-rolled Heat treated fr 50 deg. C.	soft state om hard state	Refe Soft Tem Roll Hea	annealed pered from sof ed 4 Nos. hard t treated from deg. C.	

from two reliable sources of information of recent origin. The composition of the United States sample is slightly different, as a slight amount of nickel is present to refine the grain structure. However, this does not interfere with the fabrication or heat treatment<sup>47</sup>.

Apparently there is some uncertainty for the values of the thermal and electrical conductivity in Table 3. The electrical conductivity is discussed at length later. The U. S. values are slightly lower due to the presence of a small amount of nickel. But for the present an accurate check of the efficacy of the values may be made by the Wiedemann-Franz-Lorenz law of constant ratio for the two conductivities. This determination finds the United States values in closer agreement with the law:

where, K = thermal conductivity in ca./cm.²/cm./C°/sec.
C = electrical conductivity in mhos./cm.³
T = absolute temperature.

The rolling of beryllium-copper alloys (2.25 per cent Be) from the soft quenched state improves the

the dependence of the physical properties upon the temperature and the time of the aging period, which is followed by cooling in air. When reprocessing or refabricating, the alloy is heated to 800 deg. C., and held at that temperature for 2 or 3 hrs. to restore the super-saturated solid solution structure and then quenched in cold water. The article, now in the soft annealed state, may be reworked and brought back to full strength by further heat treatment.

In hot forging or hot pressing, the alloy may be worked in the temperature range of 575 to 775 deg. C.<sup>47</sup>, dependent to some extent on the beryllium content. The article is then homogenized by annealing at 800 deg. C., prior to the usual heat treatment. Intricate parts are thus made in a soft or semi-hard condition and heat-treated back to strength.

#### Physical Properties of the Wrought Alloys

In the following paragraphs, a few of the more important physical properties of the wrought beryllium-copper alloys are emphasized:

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Electrical Conductivity: A metal added to pure copper is very detrimental to its electrical conductivity, decreasing it with increasing quantity of foreign metal. For example, 1 per cent tin lowers the conductivity of copper 50 per cent. Phosphorus and aluminum have the most pronounced effect. As the basis for further comparisons, the International Annealed Copper Standard (I.A.C.S.) will be represented by 100 per cent conductivity. This is equivalent to a resistance of 10.371 ohms per mil foot or 1.724 microhm-centimeters.

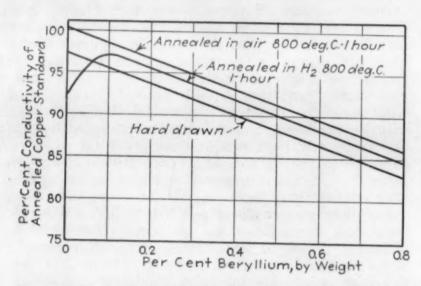


Fig. 6. Effects of Small Amounts of Beryllium on the Conductivity of Copper.

Fig. 6 illustrates the effect of small amounts of beryllium on the conductivity of copper.<sup>52</sup> For the range shown therein, each 0.05 per cent of the residual beryllium retained in the metal, reduces the conductivity approximately 10 per cent. Slightly greater than 100 per cent conductivity will be noted for pure copper annealed in air, as the presence of oxygen in small quantities improves the conductivity.

Beryllium-copper alloys exhibit a combination of mechanical and electrical characteristics not surpassed by any other alloys; immediately suggesting the application to structural parts of electrical equipment. The percentage conductivity of Table 3 compares very favorably with the current phosphor bronze alloy, which is used for springs in electrical equipment. The last mentioned alloy has a conductivity of about 7 to 10 per cent I.A.C.S. The mechanical advantage of beryllium-copper over phosphor bronze will be pointed out a little later. The electrical characteristics in Table 3 are representative of beryllium-copper that has been heat treated to secure the best mechanical properties. Further improvements in electrical conductivity (up to 40 per cent) are obtainable, though usually with a diminution of mechanical properties. Fig. 7 shows the effect of a long annealing period upon the conductivity; and quenching, followed by periods of heat treatment50. Referring to Fig. 5, there is some evidence to show the effect of long heat treatment on the mechanical properties. Prolonged heat treating results in a falling of tensile strength, though the electrical properties are improved.

A new alloy has recently been developed which offers a very high electrical conductivity, 50 per cent of the I.A.C.S.<sup>53</sup>. It is a ternary alloy of beryllium-copper-cobalt, in which only a small amount of beryllium is used. The precipitation hardening temperature was raised from 300 to 500 deg. C., which is looked upon as advantageous to the alloy as it can

keep its temper in more severe heats. Replacement of phosphor bronze in electrical parts is the chief application, as the same electrical and mechanical characteristics are obtained with one-half of the cross-sectional area.

Fatigue Limit: The beryllium-copper alloys have a high resistance to fatigue when compared with other spring materials, such as phosphor bronze, which is used in electrical contacting devices. Numerous examples cited in technical literature are given in Table 5. After the proper heat treatment for obtaining the maximum endurance and strength, beryllium-copper springs give an excellent performance, with suitable resiliency and long life. Table 5 gives the results of a number of accelerated tests on beryllium-copper springs, compared under identical conditions with standard springs.

Table 5.—Endurance of Springs

Be-Cu Alloy	Result	Comparison Alloy	Result	Refer- ence
Same size and gage as comparison	11,000,000 oper- ations, no failure	Standard bronze springs	500,000 to 1,200,000 operation fail	
Leaf springs	25,000,000; no failure	Phosphor bronze springs	400,000 vi- brations, fail	
Spiral springs	3,000,000 com- pressions, failure	Standard spiral steel spring	2,000,000 compres- sions	35
Same size and gage as comparison	10,000,000 alter- nations of stress, failure	Phosphor bronze springs	1,000,000 alterna- tions, failure	21
Tachometer con- tact springs	High fatigue	Tachometer contacts—	blab (ada-	54
Fatigue limit	35,000 to 45,000 p.s.i.	phos. bronze.  Phosphor bronze spring	high fatigue low fatigue 25,000 to 27,000 p.s.i.	e 47

However, when compared with standard high grade steel springs, the absolute fatigue limits of beryllium suffer in comparison<sup>70</sup>. J. B. Johnson in a lengthy set of tests on helically coiled springs, indicates that the fatigue limits of the high carbon steel, chromevanadium, and silico-manganese range between 70,000 to 90,000 lbs. per sq. in., while beryllium-bronze av-

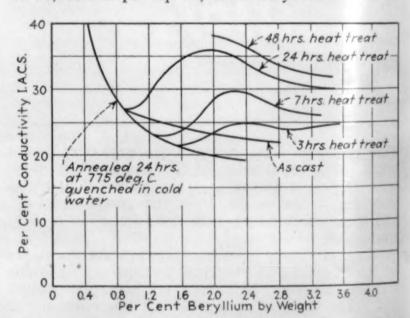


Fig. 7. Effect of Heat Treatment on the Electrical Conductivity of Beryllium-Copper.

eraged about 30,000 lbs. Notwithstanding, he arrives at the conclusion that spring steels are less efficient than beryllium-bronze with regard to fatigue limit, as the latter does not depend, to the great extent of spring steels, on the smooth polished finish of the spring wire.

Wear Resistance: Excellent wear-resisting qualities have been exhibited by beryllium-copper alloys. Re-

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cent investigations show that 0.9 to 1.5 per cent beryllium-copper makes an excellent bearing metal, wearing one-sixth as much as tin-bronzes in endurance tests25. It is well to mention at this point an important application of 2.5 per cent beryllium-copper as a bearing sleeve in a Hamilton adjustable pitch propeller55. The high strength permits bearing pressures in excess of 4000 lbs. per sq. in. High bearing loads had caused other materials to fail in a comparatively short time.

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Wear tests on an Amsler machine have served as a basis of comparison for beryllium (2.35-2.46 per cent)-copper alloy disks and a standard steel disk (0.43 per cent carbon), oil quenched from 1600 deg. F. tempered at 1100 deg. F. The steel specimen lost 0.0168 grams; the precipitation hardened copperberyllium lost 0.0001 grams; the "as cast" copperberyllium alloy lost 0.0084 grams; and the alloy heat treated for 24 hrs. suffered a heavy loss50. Contrary to these tests are the results of the American Brass Co. which state that wear resistance of berylliumcopper alloys is practically independent of heat treatment.47 In addition, it is reported that phosphor bronze wears five times as rapidly as compared to beryllium-copper in certain tests.

The wear-resisting and shock-resisting qualities of beryllium-copper are made use of in time pieces, as a bearing material 56. With further refinements in the springs (making them of beryllium-contracid) and beryllium-copper bearings, special watches were recently manufactured in Germany and compared with standard watches under severe tests. The tests consisted of dropping the watches from airplanes, and in all respects the "Beryllium watches" were superior to the standard makes.

Corrosion-Resistance: The Siemens-Konzern were the first to report that comparative corrosion resistance tests indicate that beryllium-copper alloys are fully as good as tin-bronzes, but less than aluminumbronzes. The corrosion-resistance was determined by the usual accelerated methods of measuring the loss in weight, when placed in corrosive solutions for a

period of time. Rolled sheets 1 mm. thick and 30x60 mm. were used, and the corrosive mediums were 3 per cent NaCl (sea water), 3 per cent nitric acid, and 3 per cent hydrochloric acid<sup>13</sup>. The American Brass Co. reports 2.0 to 2.25 per cent beryllium-copper having a corrosion resistance equal to deoxidized copper, under laboratory conditions of alternate immersion and salt sprays47.

In Table 6 are given some interesting comparative results of the resistance of certain alloys to oxidation at high temperatures. The gain in weight is reported as milligrams per gram of specimen, after heating for 36 hrs. at 400 deg. C. in a stream of air<sup>13</sup>.

Table 6.-Resistance to Oxidation At High Temperature

Specimen	Gain in Weight	Specimen	Gain in Weight
100% Cu 1.5% Be-Cu 2.0% Be-Cu 2.5% Be-Cu	10.2 mg. 6.1 mg. 2.05 mg. 1.37 mg.	10% Sn-Cu 12% Sn-Cu 6% Al-Cu 8% Al-Cu	4.03 mg. 2.21 mg.

(To be concluded)

#### Biography (Continued)

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#### LETTERS TO THE EDITOR

#### Re-Washed Pig for Steel

To the Editor: In your April issue, page A 19, you refer to the Perrin process of pig refining and also to Lowthian Bell as describing it in 1877 in the Journal of the Iron and Steel Institute and to Holley in 1880 in the Transactions of the A.I.M.E. The "washing" process of refining pig iron by contacting it with iron ore while melted is a forgotten art by this generation. The Brier Hill Steel Co. manufactured "washed metal" in a plant at Youngstown erected in 1883 and for years was the sole producer. They described it as "the nearest commercial approach to pure iron carbide."

Tables given showed that, with a high silicon and high manganese melted pig iron and with 10 minutes contact with ore, practically all the silicon and manganese were eliminated in the slag, while the phosphorus followed, but only about one-half the sulphur was driven off and the carbon content was little reduced. This washed pig was therefore a valuable addition in basic open-hearth practice as it helped melt the scrap without adding silicon to wear out the lining. A modification of this practice is used in making "Armco Iron" or

My U. S. patent No. 874,391 of 1907, describes a process of running a blast furnace hot to avoid sulphur in the pig iron and having manganese present with high silicon. This allows a furnace to be run with ease with no danger of high sulphur. When this iron with high manganese, silicon, carbon and phosphorus content is run through the trough to a "mixer" arrangement, the trough may be lined with ore and skimmed and more ore added in the mixer. The slag may be removed for reworking in the blast furnace to save the iron and manganese in this slag, or "forge cinder." Before much of the phosphorus is oxidized it can be poured on the scrap in a basic open-hearth which it will quickly melt and the phosphorus can be quickly removed, owing to absence of silicon.

This triplex process consisting of blast furnace, mixer and basic open-hearth steps might seem to complicate the process over the usual two steps of blast furnace and basic open-hearth furnace, but each operation is carried out under the

optimum conditions. The blast furnace, kept hot without any fear of producing high silicon iron, gives no worry to the furnaceman. The mixer acts as an equalizer and holds enough iron to make a charge for the open-hearth and the basic open-hearth melter has no worries about removing sulphur or fears of a high silicon pig to destroy the lining.

or fears of a high silicon pig to destroy the lining.

Our past industry centered itself on "tonnage" rather than quality and anything that required more time or care was tossed aside in the race for great production. We have, of late years, seen the folly of striving for greater production and realized that economical production and superior products are the demand of the times.

It may therefore be wise to look over the past and find out if we have not missed something that might be of value under modern exacting conditions.

H. O. CHUTE Chemical Engineer.

50 East 41st Street New York City

#### Liquidoid and Solidoid

To the Editor: Referring to my letter to you of recent date which you kindly published in the June number of METALS AND ALLOYS and in which I called attention of your readers to the terms "liquidoid" and "solidoid," I now find that Prof. H. M. Howe has used the word "liquidoid," as you will see by referring to page 158 of his book on "The Metallography of Steel and Cast Iron."

The reference I have in mind reads as follows: "In particular the transformations are (1) selective; (2) beginning when the cooling reaches the liquidoid GOSE." By referring to his Fig. 23, it is evident that Professor Howe ascribed to the word "liquidoid" exactly the same meaning as mine. Anyone attempting to coin a new word in metallography would do well to make a search of Professor Howe's writings.

well to make a search of Professor Howe's writings.

The term "solidoid," however, to the best of my knowledge has never been used before.

ALI

ALBERT SAUVEUR.

Cambridge, Mass.

#### A Few Chuckles

## Rusted Joints Almost Instantly Broken!

Our attention has been called to a recent "news" release as falling under the designation of "Chuckles". It lauds the superior qualities of a product of an Indiana manufacturer which "breaks the most obstinate and corroded joints almost instantly." It is in part as follows:

This product is a fluid which filters quickly into the threads of joints to be broken. Upon coming in contact with the corrosion it forms a gas which dissolves the rust into a fine powder and permits the joints to be broken easily. (Italics ours.)

It is for use on joints, bolts, studs, etc., where corrosion has made removal impossible without breaking. If applied thoroughly it will loosen these unyielding joints in two or three minutes. Only a tap with a hammer and the joint can easily be removed. It makes an ideal spring spray when mixed 5 per cent with crank case drainings.

As it is non-injurious to metal a saving of nuts, bolts

and other parts is made possible. It is also non-explosive and will burn only under intense heat. It has no lubrication value and must not be used as an additive for lubrication purposes.

#### Bessemer Steel from O- H Furnaces!

Time, June 29, 1936, page 33, quotes J. W. Davis, counsel for the Associated Press, as follows: "News is manufactured over editorial cables, while Bessemer steel may be manufactured by the open-hearth process."

Quotation from *Time*, March 23, 1936, p. 78: "The Newark, New Jersey, plant (of Westinghouse) manufactures metres."

—H. W. G.

Quotation from Fortune, March, 1936, p. 71: "You can divide all the important plastics into four groups according to whether they are derived from ...... 3. Mineral matter, chiefly phenol."—H. W. G.